国立公害研究所研究報告　第38号
Research Report from the National Institute for Environmental Studies, Japan, No. 38, 1982.

R—38—'82

Preparation, Analysis and Certification of POND SEDIMENT Certified Reference Material

Edited by Kensaku OKAMOTO

THE NATIONAL INSTITUTE FOR ENVIRONMENTAL STUDIES
環境庁　国立公害研究所

Preparation, Analysis and Certification of POND SEDIMENT Certified Reference Material

Edited by
Kensaku OKAMOTO

Division of Chemistry and Physics
The National Institute for Environmental Studies

NIES (CERTIFIED) REFERENCE MATERIALS

Pepperbush, Pond Sediment, Chlorella, Freeze-Dried Serum, Hair, Mussel (left to right)

Preface

It is my great pleasure to write a preface for the report of NIES Certified Reference Material No.2, Pond Sediment, preparation and certification of which has been completed. It is the 2nd issue of the series of our environmental standards following the 1st one, Pepperbush, and is also the second part of the report on our long-term research project of preparation of environmental reference materials.

Despite of the fact that sediment from polluted area of either pond, river or coast is one of the most important and interesting samples for the environmental studies, its certified references had been scarce. NBS of U. S. A. published a one, but was found far from a proper material because of its unusual constituents. Sediments are heterogeneous and complex materials including various organic substances, and consequently are hard to be prepared for homogeneous and lasting material.

In the spring of 1977, the presidential office of the University of Tokyo asked me to investigate the chemical components of the sediment from Sanshiro Pond, which is located at the central part of the campus, when they decided to dredge it for the hundred years anniversary of the university.

After a preliminary investigation of the sediment, we decided to make a reference material from it as the chemical components seemed to be representative of the sediments from the pond of the large modern city. We had no difficulty, at that, to obtain the proper part of the material in large sufficient quantity, since they were in the process of dredging.

Our prediction seems to be correct, as the results of the research inside of this issue has clearly indicated.

I am grateful for all members participated for the research. A particular thanks should be given to Prof. T. Kiba, who has again contributed for precise analysis of the material likewise the Pepperbush. My sincere thanks is due also to the Director, Mr. Seki of Environmental Research Center Foundation, who has taken the part of distribution of NIES Certified Reference Materials.

August, 1982
Keiichiro FUWA
Chief, Division of
Chemistry & Physics.

CONTENTS

List of Contributors

Kensaku OKAMOTO
Biochemical Analysis Section, Chemistry and Physics Division, NIES.

Yasuo IWATA
Department of Chemistry, Faculty of Science, University of Tokyo.

Haruhiko SEYAMA & Mitsuyuki SOMA
Sediment and Soil Chemical Analysis Section, Chemistry and Physics Division, NIES.

Masataka NISHIKAWA
Laboratory Services and Monitoring Section, Chemistry and Physics Division, NIES.

Cameron W. McLeod
Biochemical Analysis Section, Chemistry and Physics Division, NIES
(Present address) Sheffield City Polytechnic, Pond Street, Sheffield,
S1 1WB, U.K.

Takejiro TAKAMATSU
Soil Environment Section, Water and Soil Environment Division, NIES.

Munetsugu KAWASHIMA
Department of Chemistry, Faculty of Liberal Arts and Education,
Shiga University, Otsu, Shiga.

Rokuji MATSUSHITA & Mutsuo KOYAMA
Research Reactor Institute, Kyoto University, Sennan-gun, Osaka.

Editor's Note

International standards organizations such as the International Union of Pure and Applied Chemistry (IUPAC) and the International Standards Organizations (ISO) have recommended the use of the term "Certified Reference Material" along with the abbreviation CRM to describe primary reference materials. According to the above recommendation the National Institute for Environmental Studies (NIES) will use the term "Certified Reference Material" for such materials produced by NIES.

CHAPTER I

Sediments in Environmental Analysis

K.Okamoto

1. Introduction

In recent years, an increasing number of analyses of a wide variety of environmental samples, such as the atmosphere, water, soil and biological materials, have been carried out in laboratories of universities, national and local govermental organizations, and independent institutions. The main purpose of such analyses are to indicate the actual state of environmental pollution, detect the onset of adverse changes in the environment and to understand the origin and mechanism of the phenomena. In order to characterize the distribution of pollutants in the environment, and/or to detect abnormal values in a time series over a long period, a large number and a wide variety of environmental samples are collected and analyzed. In many cases substances to be monitored include heavy metals, organic compounds and toxic gases in diverse environmental samples.

Systematic research concerning the movement and accumulation of pollutants of both inorganic and organic nature in the total environment requires highly reliable analytical methods to warrant meaningful results. Despite the remarkable progress experienced in the field of instrumental analytical techniques during the last decade, data on elemental analysis of environmental and biological materials are still considered unreliable. In order to correctly evaluate the state of the environment, "accurate" analytical data on the properties under measurement are first of all required. The appearance of adverse changes in environmental quality can then be noted based on the analytical values collected over long periods.

Policy decisions on environmental problems also require "accurate" analytical data in order to judge whether the problem should be controlled and improved according to the relevant law. Unfortunately the reliability of data provided by laboratories engaged in such projects is open to question since there is a lack not only of reference methods of analysis but also of appropriate certified reference materials. In many instances, therefore, it is not possible to properly assess analytical data and to decide whether the data constitute an environmental problem.

If a measurement process is to be meaningful, then the data obtained should be both precise and free of systematic error within acceptable uncertainties of end-use requirements. Additional requirements for measurement processes, such as wide dynamic range, high sensitivity, or rapid operation, might also be desirable. However, such requirements are not necessary in achieving accuracy but rather represent practical considerations. The establishment of compatible accuracy-based chemical measurement systems is becoming increasingly essential for environmental analysis[1)].

There are a number of different ways of achieving measurement compatibility and transferring accuracy between two or more laboratories. The ways usually employed to achieve accurate chemical measurement are; 1) to use accurately characterized reference methods, and 2) to use accurately characterized reference materials. A reference method is a method that has had its accuracy rigorously demonstrated through experimental validation. Reference methods provide a mechanism for achieving measurement compatibility. Reference methods are being increasingly used in conjunction with reference materials to assure measurement compatibility.

A second way to achieve measurement compatibility is through the use of reference materials as transfer devices. Reference materials are well -characterized, stable, homogeneous materials, produced in quantity and having one or more physical or chemical properties experimentally determined within stated measurement uncertainties. Certified reference materials are reference materials having properties certified by a recognized national standard laboratory or standard agency. Certified reference materials are certified using the most accurate and reliable measurement techniques available consistent with the end-use requirements[1-3)].

In Japan, the reference methods adopted by the Japanese Industrial Standard and the Environment Agency have been used for the analysis of many environmental samples. However, the use of such reference methods are restricted to the determinations of certain elements, certain organic compounds, and to special materials. On the other hand, the number of environmental certified reference materials has been limited. Since many of the rapid instrumental methods such as x-ray fluorescence are subject to interferences (matrix effect), the CRM matrix should be similar to that of normal specimens being analysed by such techniques. The degree to which a reference material may be used to establish accuracy or compatibility depends on how closely it corresponds to the specimen being analysed.

In areas such as environmental or clinical analysis where "real world" specimens may be exceedingly complex and variable, a wide variety of certified reference materials are urgently required in order to give assurance to the analytical results. It is mainly for this reason that the National Institute for Environmental Studies (NIES) has recently initiated a certified reference material (CRM) programme. This introductory chapter describes the chemical characteristics of environmental samples and discusses the concept of the CRM within the framework of environmental analysis. The current status of the CRM programme at NIES is also summarized.

2. *Characteristics of Environmental Samples*

First, we should consider the characteristic properties of environmental samples from the view point of chemical analysis[4)]. Environmental samples are composed of many elements and compounds, and sometimes different phases co-exist. The complex composition of the materials may inhibit accurate analysis of the desired components. For example, the co-existence of major elements may sometimes cause matrix interference, increasing or decreasing the measured value. Also the chemical composition of environmental samples differ greatly so that the appropriate analytical method should be selected considering the matrix of the analyte. Very often the analytical procedure requires a chemical separation of the components of interest from the original material.

Concentrations of pollutants may vary from ng/g levels to several hundreds of ug/g so that the selection of an appropriate analytical method for the concentration level expected is an essential point. For the determination of low level concentration, the handling and pretreatment of sample must be carefully performed taking care to prevent contamination or loss. Special facilities such as a clean laboratory are of value to minimize contamination from air particulates. Reference methods of analysis for determinations at the ng/g or pg/g level are required and, in spite of many efforts, few such methods have been established.

It is well known that the essentiality and toxicity of an element are closely related to not only the total amount of a metal but also the chemical forms of the element. An important requirement, therefore, is that analysis involving chemical speciation should be performed to evaluate the quality of the environment. The chemical forms of an element may be exceedingly complex, and the existence of various oxidation states, and chemical binding to low molecular weight compounds such as a metallo-organic substance and/or high molecular weight compounds such as a metalloprotein should be considered. The identification and determination of each chemical species invariably requires a preliminary separation of the component of interest prior to determination. The determination of total amounts of elements has been extensively carried out for environmental studies, but it is much more difficult to determine the chemical forms of elements. The development and improvement of separation techniques which cause little denaturation of the *in vivo* components are required. This situation is also true of organic compounds which have many derivatives.

Biological and geological samples, characteristically, are heterogeneous in composition and pollutants may be distributed heterogeneously according to their physico-chemical properties. In the animal body, halogenated pesticides like BHC have a tendency to concentrate in the fatty tissues, and therefore, concentrations differ according to the sites analysed. It is also important to specify whether results are expressed on a "total" or "fat" basis. In this case, the units to express the concentrations should be carefully selected to provide the most meaningful results. When we intend to express concentrations on a total basis, complete homogenization of the sample is necessary prior to analysis. It is rather difficult, however, to prepare homogeneous samples for some types of materials such as human hair or fish.

Environmental samples may not be stable indefinitely. During transportation of the sample from the collection point to the laboratory, substantial changes in the amounts and chemical forms of pollutants and media may occur. Care must be taken to select the appropriate sampler, container and preservation procedure. Generally environmental samples can readily undergo physiological and chemical changes due to microbial activity. Therefore, the most suitable preservation method such as acidification, freezing or sterilization should be applied to the sample.

As mentioned above, many features of environmental samples make accurate analysis difficult and the proper selection of the analytical methods and techniques is required. Analytical methods should be selected considering not only the nature of the sample but also the sensitivity and inherent accuracy of the analytical technique. The facilities and instruments of a laboratory and the experience of a scientist are also factors which determine the analytical methods and techniques to be used.

3. *Features of Sediment Samples*

Sediment, a matter that settles out at the bottom of natural water systems, consists of various sizes of rock debris, sands and clays formed by weathering action on parent rocks. Although rock material is clearly the dominant initial source of a sediment, organic substances derived from decaying vegetation are also important components of the sediment. For example, initially the trace element composition of a sediment will be that of its geological parent material, however, with time the composition will change progressively under the influence of deposited materials of both inorganic and organic nature.

Sediments in large lakes reflect the nature of overlying waters at the time of deposition because of their capacity to incorporate organic and inorganic constituents during transport and deposition. Therefore, lake sediments provide both a record of past climatic and geological events and an indication of the activities of man in the surrounding watershed. Under ideal conditions where almost no physical and biological disturbances have occurred, sediments can be an invaluable historical record of environmental pollution, ice samples in the polar areas being a notable example. Actually, a number of investigations have been successfully carried out to detect environmental changes in a time series over a long period, using "sedimentary columns" taken from the bottom surfaces of lakes and seas.

Sediments are an integral part of the cycling of elements in water. Heavy metals in water may precipitate on the bottom surface due to the changes in their chemical forms and through their incorporation by biological materials. The accumulation of heavy metals may also occur by the actions of adsorption and ion exchange on mineral surfaces of the sediment. In parallel, a slight release of heavy metals from the sediments to overlying water may proceed mostly under the influence of microorganism activities. The levels of heavy metals in sediments are, therefore, generally much higher than those in overlying water. The elevated level of a metal in sediments usually makes the determination of the metal relatively easy, even in the case that the metal in the water may be expected to be below detection capabilities of analytical techniques. This is one of the advantages that sediments offer to environmental analysis. This accumulation capability of the sediments is also true of organic compounds, particularly so for the analysis of man-made organic compounds, where the synthetic compound may suddenly be detected at a point in time corresponding to manufacture and usage, and with passage of time gradually increasing amounts have been observed. As mentioned above, sediments directly reflect the surrounding environments and thus can be one of the most important samples in environmental analysis.

Organic matter appears to be an important factor in considering the nature of sediments. The relative influence of organic matter on retention and/or complexation of heavy metals should be evaluated. The ability of stabilized organic matter in sediments to form complexes is generally attributed to humic acid and fulvic acid. The influence of organisms on trace element distribution may be significant in many cases. Plankton and excretory products of fish are a concentrated source of many trace elements and may promote their transport to sediments. The efficiency of trace element transport from water to sediments depends in part on the rate of decay of the dead organism or excretory product. Microbial activity in the surface of sediments facilitates further decay at the sediment-water interface and may result in increases in trace element concentrations in the sediments. Trace elements show a marked affinity for organic materials with the formation of complexes which may be the predominant soluble form of the element in sediments. Many of such chemical reactions are undoubtedly mediated by microorganisms. A sediment is, therefore, a very dynamic system and the balance of chemical equilibrium is often very sensitive to slight chemical, physical or biological change.

On the other hand, such exceedingly complex features of sediments very often inhibit accurate analysis of sediment samples. For example, the distribution of elements varies with the particle sizes of sediments, therefore, grinding and homogenization of the sample may be required prior to analysis. Organic matter present in sediments such as humic acid has a tendency to form metallo-organic complexes some of which may be easily lost by sample heating, so that an appropriate drying method should be selected for the determination of such volatile elements or compounds. Microorganisms in sediments release various kinds of metabolites which convert metals to soluble and/or organo-metallic form, therefore, special care should also be taken to specify the chemical forms of the element of interest. Although many studies on trace elements are concerned with only total levels, the environmental significance of the results may be clear only when knowledge of the chemical form of the element is available. Special attentions have also to be paid to the changes in pH and Eh which are important factors in determining the physical and chemical states of the element in sediments.

From the viewpoint of elemental analysis, we should first decide whether the analytical values for elements in sediments are expressed on a "total" or "extraction" basis. Total analysis by standard alkali fusion or acid decomposition using hydrofluoric acid has been extensively used in the fields of geochemistry and analytical chemistry, while the extraction and determination of elements using appropriate extractants such as 0.1 M hydrochloric acid or EDTA have been employed in the areas of soil chemistry and plant nutrition. The choice of the proper method has been made considering the significance of the respective analytical method in the corresponding field. For example, extraction methods have been employed in order to correlate plant growth to concentrations of metals available to plants and also to improve our understanding of the chemical properties of soils. From the standpoint of chemical analysis, however, the extraction methods have a disadvantage that extraction efficiency varies with the nature and concentration of extractant and is dependent on experimental conditions. In the field of reference materials, in contrast, the total analytical value is definitely required. A well-established analytical method having good recovery, reproducibility and accuracy should be applied to the analysis of reference materials. Therefore, total analysis by alkali fusion or acid decomposition has been used in all cases for the certification of reference materials. In this report the analytical values for Pond Sediment are expressed on a "total analysis" basis, unless otherwise noted.

Sediments are, characteristically, heterogeneous materials consisting of various kinds and sizes of mineral materials and organic materials, so that grinding and homogenization should be carefully performed prior to analysis. The presence of organic matter in sample solution usually inhibits the accurate analysis of elements, therefore, the addition of perchloric acid as well as hydrofluoric and nitric acids is very often required in order to destroy organic materials completely. Certain elements are bound to organic matters, forming metallo-organic complexes which may be vaporized in part during heating, thus for the determination of such metals appropriate drying conditions should be selected to prevent losses of the elements. All analytical values for reference materials are usually expressed on a dry weight basis. For volatile elements such as mercury and selenium, drying should be done on separate samples other than the sample for analysis.

The major elements in sediments are Si, Al and Fe, the levels of these matrix elements are usually 20-30 % of Si, and 5-10 % of Al and Fe. In contrast, elements of environmental interest, for instance Cd, usually exist at concentrations below 1 μg/g, being five orders of magnitude lower than those of matrix elements. Therefore, proper sample pretreatment such as chemical separation and concentration of the objective element has been required to remove interferences by matrix elements. Solvent extraction techniques have most often been applied to remove the interfering elements and to concentrate the element under measurement. Co-precipitation or ion exchange technique has also been used for such purposes.

4. *Sediment Reference Materials*

In the field of geochemistry, many rock standard materials have been issued by the U.S. Geological Survey and other relevant organizations5,6). In Japan the rock standards such as JG-1, JB-1, have been distributed by the Geological Survey of Japan7).

Sediment samples are much more complex in composition compared with rock materials as mentioned above, so that the analyses of sediments are generally more difficult than those of rock samples. The Environment Agency of Japan has recently performed a series of quality control exercises for local legislative purposes using "Kanto Loam" and "River Sediment" samples. The results of the programme were summarized for the determinations of Cd, Cr and As8). In this study, however, some inconsistencies in the analytical values for some elements existed.

Although a large number of sediment analyses have been carried out all over the world, there are many analytical problems associated with sample handling and analysis. These situations stress the importance and need for sediment CRM in environmental analysis.

Table I shows the sediment reference materials currently available or being prepared at various organizations throughout the world. The National Bureau of Standards (USA) has issued "River Sediment" SRM in which 13 elements are certified[9]. This material was collected from the heavily-polluted area in Indiana of the United States and contains approximately 3 % of Cr. At NBS, "Estuarine Sediment" reference material is now being prepared. The International Atomic Energy Agency (IAEA) is distributing "Lake Sediment" reference material, in which the recommended values are given for 28 elements. The Community Bureau of Reference (BCR) in Europe has prepared "River Sediment" and "Lake Sediment" reference materials, and the certification of these samples is now underway[10].

Table I

Sediment Reference Materials

River Sediment	NBS	1645
Estuarine Sediment	NBS	1646
Pond Sediment	NIES	No.2
Lake Sediment	IAEA	SL-1
River Sediment	BCR	S-1
Lake Sediment	BCR	S-2
Marine Sediment	NRCC*	MESS-1
Marine Sediment	NRCC	BCSS-1

Despite the efforts to prepare and certify sediment reference materials at various national and international organizations, the number of sediment certified reference materials has been limited so far. Considering the importance of and great demand for a new type of sediment certified reference material in environmental analysis, NIES has recently prepared and certified "Pond Sediment" (certified reference material No.2). The preparation and analysis of Pond Sediment will be described in detail in the following chapters.

Table II shows the elemental composition of Pond Sediment and also includes, for comparison, the elemental content of River Sediment NBS SRM[9], Palace Moat Sediment (Tokyo)[11], and the average concentrations in the earths crust and soils[12]. Pond Sediment contains a higher concentration of heavy metals compared to the average values of soils. However,

---

* National Research Council of Canada

Table II

Elemental Composition of Pond Sediment and Comparison with Other Environmental and Geological Data

Element	Pond Sediment	River Sediment[9)	Palace Moat Sediment[11)	Mean Crust[12)	Median Soil Content[12)
			values in %		
Si	21	24.0		27.7	33.0
Al	10.6	2.20		8.20	7.10
Fe	6.53	11.3	4.7	4.10	4.00
Ca	0.81	2.90		4.10	1.50
			values in $\mu g/g$		
Ti	6400			5600	5000
Mn	770	785	750	950	1000
Zn	343	1720	1400	75	90
Cu	210	109	300	50	30
Pb	105	714	300	14	35
Cr	75	29600	100	100	70
Ni	40	45.8	45	80	50
Co	27	8	18	20	8
F	285			950	200
Hg	1.3	1.1		0.05	0.06

in general, the elemental concentrations of Pond Sediment are not as high as those of NBS River Sediment. In particular, NBS River Sediment contains Cr at the percent level which is anomalous for a typical soil or sediment. A comparison of metal contents between Pond Sediment and Palace Moat Sediment (Tokyo) shows that the compositions are similar, and therefore, Pond Sediment certified reference material may be considered as a typical sediment sample found in the vicinity of a large city[13).

5. Present Status of the Environmental CRM programme at NIES

The National Institute for Environmental Studies has recently instigated a certified reference material programme, the objective being the preparation and certification of environmental standards, to serve the needs of environmental scientists and laboratories. Various categories of certified reference materials can be considered, for example, elements, gases and organic compounds. At present, our CRM programme is restricted to the preparation of environmental samples and certification of elemental composition.

Table III

NIES Certified Reference Material (CRM) Programme

Pepperbush	(Botanical)	Certified
Pond Sediment	(Geological)	Certified
Chlorella	(Biological)	Analysis in progress
Human Serum	(Clinical)	Analysis in progress
Hair	(Clinical)	Analysis in progress
Mussel	(Biological)	In preparation

Table III shows the present status of the CRM programme at NIES. The first CRM is a botanical sample, Pepperbush, the preparation, analysis and certification of which have been described[14). The most typical characteristics of Pepperbush relative to the botanical SRMs issued by NBS are the high concentrations of manganese, zinc, cobalt, nickel and cadmium. The second CRM issued is a geological sample, Pond Sediment, the preparation, analysis and certification of which are described in detail in this booklet.

The third reference material is a biological sample, Chlorella, a typical green algae which are widely distributed in lakes, river and ponds. In recent years, environmental pollution of the aqua system by heavy metals and organic compounds is having adverse effects on animals, plants, fish and also on human health. An urgent requirement, therefore, is to identify and monitor such substances in the hydrosphere. Besides its value for monitoring water pollution, Chlorella reference material will also be of use in basic studies since chlorella has already been used extensively as a research material.

It is well known that certain inorganic elements are required for normal growth and development of the human body and, at present, about 26 elements are considered to be essential or beneficial for life. Diseases have been related to abnormal concentrations (deficiencies and excesses) of major, minor and trace elements in fluid and tissue. It is clear that there is a great need for human fluid and tissue certified reference material and, therefore, Freeze-dried Serum reference material (NIES No.4) has been prepared for trace metal analysis. Human hair is an important sample for monitoring metal accumulation in the human body so that Hair (NIES No.5) has also been prepared as a reference material for trace element analysis. It should be realized that concentration levels for many essential/non-essential elements in clinical samples are extremely low and reliable methods of analysis are not as yet established, and the certification of clinical reference materials is by no means an easy task. These reference materials will be certified and distributed from NIES in the near future.

In the field of reference materials, there may be some categories where the numbers of certified reference materials currently available have been limited. They are "animal tissue," "fish" and "shell" samples. NBS has been distributing "Bovine Liver" and "Oyster" SRMs for elemental analysis, furthermore, there are great demands for new type reference materials of such categories. At NIES, "Mussel" reference material is now being prepared. Mussel is a shell widely distributed in the sea all over the world and has been extensively used as a material to monitor environmental pollution by heavy metals and organic compounds15). Therefore, mussel may occupy a more important status than oyster from the viewpoint of environmetal analysis. Soft parts of mussel were ground by cryogenic grinding, freeze-dried and homogenized to be prepared as a reference material.

As mentioned earlier, the certified reference material programme at NIES has been oriented to the preparation of diverse environmental samples and certification of elemental composition. Clearly there is a parallel need for certified reference materials where the contents of various organic compounds have been certified. Although there exist many difficulties with respect to the preparation, homogeneity, preservation, and analysis of the "organic" certified reference material, research for making such CRMs is to be carried out. In the case of Mussel sample, special consideration has been given to preparation so that the sample can also be used for the determination of organic compounds.

References

1) Uriano,G.A. & Gravatt,C.C. (1977): *CRC Crit. Rev. Anal. Chem.*, 6,361
2) Cali,J. P.,*et al.* (1975): The role of standard reference materials in measurement systems, *NBS monograph* 148.
3) Cali,J. P. & Reed,W. P. (1976): Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis. *NBS Special Publication*,442, p.41-63
4) Ambe,Y. (1980): Preparation, Analysis and Certification of PEPPERBUSH Standard Reference Material, *NIES Research Report* No.18, p.1-6
5) Franagan,F. J. (1973): *Geochim. Cosmochim. Acta*, 37, 1189
6) Franagan,F. J. (1974): *Geochim. Cosmochim. Acta*, 38,1731
7) Ando,A., Kurasawa,H., Ohmori,T. & Takeda,E. (1974): *Geochem. J.*, 8, 175
8) Environment Agency of Japan (1981): *Kankyo Sokutei Toitsu Seido Kanri Kekka;* Yamagata N. (1982): *Bunseki Kagaku*, 31,T1.
9) Certificate for Analysis, River Sediment (1978): NBS, Washington D.C.
10) Muntau,H. (1980): *Production and Use of Reference Materials, Bundesanstalt fur Materialprufung*, Berlin, p.185-218
11) Goldberg,E. G.,*et al* (1976): *Geochem. J.*, 10, 165
12) Bowen,H. J. M. (1979): Environmental Chemistry of the Elements, Academic Press, London, pp. 36, 60
13) Iwata,Y., Matsumoto,K., Haraguchi,H., Fuwa,K. & Okamoto,K. (1981): *Anal. Chem.*, 53, 1136
14) Okamoto, K. (ed) (1980): Preparation, Analysis and Certification of PEPPERBUSH Standard Reference Material, *NIES Research Report No.18*
15) Goldberg, E. D. (1975): *Mar. Pollut. Bull.*, 6. 111

CHAPTER II

Preparation of Pond Sediment

K. Okamoto and Y. Iwata

1. Introduction

Against the background for the need to improve the quality of analytical results in environmental analysis, the importance of reference materials during the last decade and particularly in the environmental sciences has been increasingly recognized. Although various kinds of certified reference materials (CRMs) have been issued by national and international standards organizations, the number and diversity of environmental CRMs currently available has not been able to satisfy demand. Undoubtedly, sediment is one category of CRM which has not received sufficient attention by standards organizations.

Considering the significance and importance of sediment reference materials in environmental analysis, the National Institute for Environmental Studies has chosen a sediment as the second CRM to be issued by the institute. Sanshiro pond within the grounds of the University of Tokyo was selected as the site for collection. In May 1977, when the pond was being dredged during cleaning operations, large amounts of salvaged sediment were taken and transported to the institute for preparation of "Pond Sediment" CRM.

Since Sanshiro pond is located in the center of Tokyo, it is expected that the pond has been exposed to environmental pollution such as exhaust gases from automobiles and factories. The pond has not received industrial or public waste water and, therefore, atmospheric particulates may have been the major source of environmental pollution. A preliminary geochemical analysis of the Sanshiro pond sediment indicated that the material consisted mainly of rock-forming minerals, clay minerals and organic matter as well as other typical sediments or soils1). The sediment also contained a large quantity of volcanic ash called "Kanto-loam", which is a result of past volcanic emissions. With respect to elemental composition, the characteristic features of Pond Sediment when compared to the earth's crust, a typical soil and NBS River Sediment SRM (previously discussed in part in Chapter I, page 9) are summarized as follows:

(1) The concentrations of major and minor elements in Pond Sediment such as Si, Al, Fe, Mg, Ca, Na, K, Ti and Mn are similar to that for typical soils and geological materials.

(2) The concentrations of the trace elements Zn, Cu, Pb, Cd and Hg in Pond Sediment are significantly higher than that found in the earth's crust and in typical soils, whereas similar concentrations were found for Cr, Ni and Co.

(3) Pond Sediment contains considerably higher amounts of C, S and N, which are mainly derived from organic matter, compared to the earth's crust.

(4) The elemental composition of Pond Sediment is similar to that of NBS River Sediment SRM except for a few elements such as Cr, Zn and Pb, which are anomalously high in the latter.

Technical considerations associated with the preparation of the reference material included speedy sample treatment and care to prevent contamination, so that the nature of the prepared sample was as similar to that of the original material as possible.For example, non-metallic apparatus were used in preparation whenever possible. A preliminary study using a small amount of the sediment gave encouraging results on sample homogeneity2). Finally, the Sanshiro pond sediment was judged suitable for preparation as a sediment reference material.

2. *Preparation of Pond Sediment*

The procedure used for the preparation of Pond Sediment was similar to that adopted for Pepperbush CRM3). An outline of the sample preparation is illustrated in Fig. 1.

a. Sampling and Pretreatment

In May 1977, the sediment (about 500 kg, fresh weight) was collected from the bottom surface at the center of Sanshiro Pond to a depth of one meter. A small quantity of distilled water was added initially to a batch of the sediment and the mixture was stirred well. Then the wet sample was sieved through a nylon sieve (2 mm) to remove gravel and leaves.

b. Drying

The wet-sieved material was filtered by means of suction with a Buchner funnel (30 cm ϕ) to remove interstitial water, and it was air-dried on a filter paper (Toyo No.2) at room temperature for about 2 weeks. About 70 kg of the dried pond sediment was obtained.

Since sediments generally contain relatively high amounts of volatile and complex components, elemental composition and chemical form may change during the drying of wet sediments. The following drying methods were therefore examined: (1) air-drying at room temperature (2-3 weeks), (2) oven-drying at 80℃ (24 hrs), (3) freeze-drying (24 hrs). The results of such investigations with respect to elemental composition have been described in

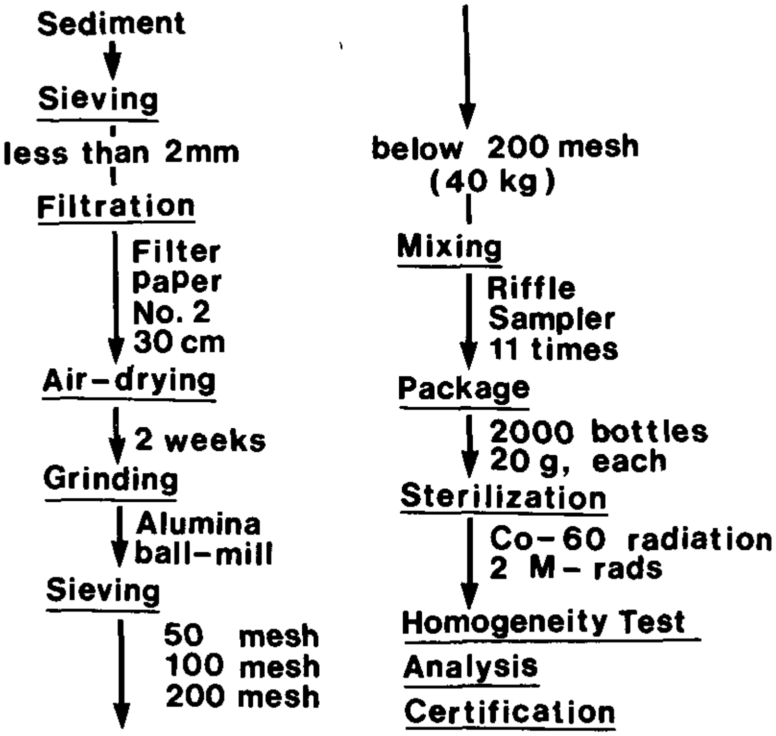


Fig 1. Outline of the preparation of Pond Sediment

detail4), and in summary no significant differences in elemental composition for the three drying methods were detected. In particular the concentrations of Hg and organic matter (estimated from ignition loss) were consistent for the three methods. The freeze-drying method is not convenient for sample treatment on a large scale and it is also known that some clay minerals change their structure on heating. Therefore, and air-drying method was selected for the sediment.

c. Grinding and Sieving

The air-dried sediment was ground for about 1 hr in an alumina ball-mill (95 % Al_2O_3, 7 liter), which had previously been used for grinding a small portion of the sediment to minimize contamination. As reported by Ando[5], metallic contamination from alumina ball-mills has been considered to be not serious. The pulverized samples were placed on a set of the nylon sieves arranged as follows: a 50-mesh (297 μm) nylon sieve (top), a 100-mesh (151 μm) one (second), a 200-mesh (71μm) one (third), and a reservoir made of polyvinylchloride (bottom). The apparatus was then vibrated mechanically for 15 min.

In order to estimate the homogeneity of the various fractions (above 50-mesh, 50-100-mesh, 100-200-mesh, below 200-mesh), X-ray fluorescence, atomic absorption and inductively coupled plasma emission analyses were performed for certain elements and the relative standard deviations of analytical values were calculated for each element[2,4]. Improved homogeneity was associated with the finer grain sizes. Accordingly, the material which passed through a 200-mesh sieve exhibited the best homogeneity and was most suitable for the preparation of the reference material. Besides consideration of homogeneity, dried sediments ground to powder of mesh size 200 have been most frequently employed in routine analyses. Consequently, the finest part (below 200-mesh) of the sediment was selected for further processing.

These analytical techniques were also used to determine the elemental distributions of the four different grain sizes. The elemental compositions of the various fractions were significantly different as follows[4]: The finest part contained higher concentrations of organic matter and trace elements such as Zn, Cu, Cr and Co relative to the coarser fractions. In contrast, the finest fraction contained lower concentrations of elements indicative of silicate rocks such as Si, Mg, Ca, K and Na, and also contained less amounts of silicate minerals such as quartz and feldspar, compared to the other larger fractions.

These findings are consistent with XPS data (see Chapter III) and suggest that trace elements and organic matter are adsorbed on the surface of fine particles, possibly clay minerals and free oxides of Si, Al, Fe and Mn. In addition to adsorption effects, co-precipitation effects may also be taken into account. Actually, Tessier *et al*[6] reported that fractions of Fe-Mn oxides and organic matter have a scavenging effect and, as a result, have an ability to concentrate trace elements.

Fig 2. Riffle sampler.

d. Mixing and Sterilization

The sediment powder (about 40 kg) that passed through a 200-mesh sieve was divided into two parts with a riffle sampler (JIS No.2) made of polyvinylchloride. The powder was piled up into two layers and again divided by passing through the riffle sampler. The sediment sample was homogenized by repeating this procedure 11 times. This homogenized sample, which constituted the reference material, was packaged in about 2,000 acid-washed glass bottles (about 20 g each). The bottled samples were sterilized by ^{60}Co radiation of 2 Mega-Rads at the Japan Atomic Energy Research Institute (Takasaki, Japan) to minimize deterioration due to biological activity.

It is essential for geochemical CRMs to have a shelf-life of at least 5 to 10 years and therefore special care should be taken for the preservation of sediment reference materials. Sediments are substantially heterogeneous materials containing microorganisms, therefore, an appropriate sterilization of the sample must be carried out to eliminate microbial activity which may cause loss or chemical conversion of elements. By the application of ^{60}Co γ-ray radiation, Pond Sediment can be maintained microbe-free until the bottle is opened.

3. *Assessment of Homogeneity*

In the preparation of a reference material it is essential that the prepared samples are homogeneous within the accepted range of end-use requirements. Although homogenization of Pond Sediment was attempted through procedures such as grinding, sieving and mixing, an assurance of homogeneity of the material must be given to establish it as a reference material. Since Pond Sediment is a reference material for elemental composition, homogeneity can be assessed by establishing the variation of elemental content for samples selected randomly. The variation of metal content when measured by an analytical technique at one laboratory will include sample variability, digestion error and measurement imprecision. Non-destructive multielement analysis techniques, such as neutron activation and X-ray fluorescence, are preferable for homogeneity testing, because the error associated with sample dissolution can be neglected. At present, however, neutron activation analysis has not been applied to homogeneity assessment because of the limited availability of reactor facilities. A preliminary study by X-ray fluorescence also revealed that the measurement imprecision of the analytical technique was larger than the acceptable range for this purpose.

For the assessment of homogeneity of Pond Sediment, an acid-dissolution followed by atomic absorption analysis was finally adopted. Eleven bottles were selected randomly using a random number table from the lot of 2,000 bottles. The content of each bottle was divided into two parts and analysed independently at both NIES and the University of Tokyo.

At NIES, three portions (1g, each) of the sample were taken from each of the eleven bottles and dissolved as described in Chapter IV. Table I shows the results for the homogeneity test (by the analysis of variance) performed at NIES. The analysis of variance technique allows the testing variation and the sampling variation to be separated and their magnitudes estimated$^{7)}$. The analytical values determined by AAS are given for Zn, Cu, Pb, Ni and Co in Pond Sediment. The variations *within* bottles (experimental error) in terms of the relative standard deviations (RSD) were between 0.87 and 3.2%, while the variations *between* bottles (sample homogeneity) were less than 1.0% for each element shown in Table I. These results indicate that the variation associated with the sample variability was much smaller than the analytical error.

At the University of Tokyo, triplicate samples (2g, each) taken from each bottle were dissolved with a mixture of nitric, hydrofluoric and perchloric acids on a hot plate (200 °C). Finally, hydrochloric acid (1:1) was added to dissolve the residue and the solution volume was adjusted to 100 ml. The sample solutions were used to determine Cu, Mn, Pb and Co by AAS using an air-acetylene flame. Homogeneity was checked by the analysis of variance (two-way layout method$^{7)}$, and the results are given in Table II. The results

Table I

Homogeneity Test for Pond Sediment
(NIES)

	Zn	Cu	Pb	Ni	Co
$\overline{X}$ (μg/g)	341	209	106	35.6	29.2
$\sigma_W/\overline{X}$ (%)	0.87	1.2	3.2	1.6	1.8
$\sigma_B/\overline{X}$ (%)	0.52	0.72	0.0	0.90	0.71

The values are based on the material dried at 110 °C for 4 hrs in an oven. ($\overline{X}$): grand mean; ($\sigma_W/\overline{X}$): variation *within* bottles (i.e. experimental error) and ($\sigma_B/\overline{X}$): variation *between* bottles (i.e. sample homogeneity), expressed as the relative standard deviation.

Table II

Homogeneity Test of Pond Sediment Samples[a]
(University of Tokyo)

	Cu	Mn	Pb	Co
$\overline{X}$,[b] μg/g	220	721	103	29.1
$\sigma_A/\overline{X}$[c] (%)	1.3	0.75	1.1	1.4
$\sigma_D/\overline{X}$[d] (%)	1.7	2.3	3.1	3.2
$\sigma_E/\overline{X}$[e] (%)	2.1	0.90	1.8	2.4

[a] Analytical data are expressed as the dry weight. Samples were dried at 110°C for 4 h in an oven. [b] $\overline{X}$, average concentration. [c] σ_A, homogeneity of samples. [d] σ_D, error of digestion. [e] σ_E, error of measurement.

of the F-test show Pond Sediment to be homogeneous. The expected values (RSD) for homogeneity of Cu, Mn, Pb and Co were 1.3, 0.75, 1.1 and 1.4 % respectively, whereas those for digestion error of Cu, Mn, Pb and Co were 1.7, 2.3, 3.1 and 3.2 %, respectively[8]. It is evident from these data that Pond Sediment satisfies homogeneity criteria for a reference material.

4. *Thermogravimetric Analysis of Pond Sediment*

Analytical values for reference materials are usually expressed on a dry weight basis, therefore, an appropriate description of a drying method(s) should be included. In the analyses of rock reference materials oven-drying at 105-110℃ has most often been used, while for drying of biological reference materials a freeze-drying method has often been employed to avoid denaturation of these materials by heating. Since Pond Sediment contains a relatively high amount of organic matter (approximately 5 % as carbon), a drying condition(s) prior to analysis should be carefully decided.

A thermogravimetric technique was employed in order to monitor the weight change of Pond Sediment during heating. First, a thermogravimetric change of Pond Sediment (51 mg) was recorded with increase of sample temperature from room temperature to 500℃ at a rate of 0.5℃/min. A decrease of the sample weight gradually occurred with increasing temperature, reflecting the loss of moisture. Many rock materials generally show a plateau region near 100-110℃, whereas a level-off of moisture loss around these temperatures was not observed for Pond Sediment. There was a slight continueous decrease of the sample weight between 100 and 110℃, indicating that Pond Sediment is more complex in moisture-loss behaviour than rock materials. This phenomenon is possibly connected with the relatively high amount of organic matter in Pond Sediment. Above approximately 250 ℃, a rapid decrease of the sample weight occurred due to both loss of water of crystallisation and combustion of organic matter.

Second, a thermogravimetric pattern of Pond Sediment was recorded when the sample temperature was increased at a rate of 2℃/min until 110℃ and then held at 110℃ for 4 hrs. As shown in Fig 3, a gradual decrease of the sample weight is observed until the temperature reaches 110℃ (about 1.5 hr under this condition). When the sample temperature is held at 110℃, the sample weight has almost levelled off, ranging from 10.3 % moisture loss at the beginning (1.5 hr from the start) to 10.5 % at the end (5.5 hrs). This result indicates that oven-drying at 110℃ yields a constant weight of sample after heating for more than about 2 hrs. Also, the moisture loss (at 110℃, for 4 hrs in an oven) obtained by collaborative work (30 laboratories) was 11.1±0.3 % (mean±standard deviation), which gives further support that the

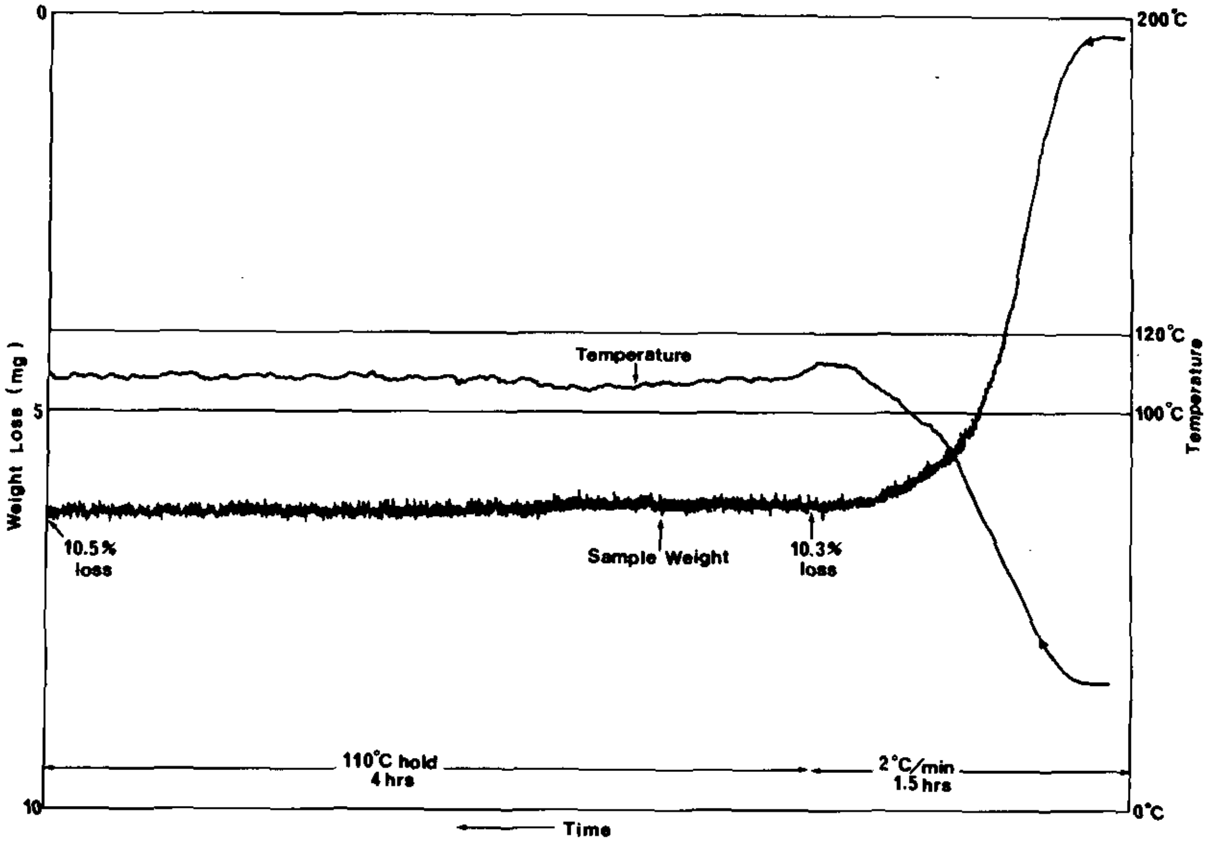


Fig 3. Thermogravimetric analysis of Pond Sediment sample (60.2 mg); the temperature was increased from room temperature to 110 °C at a rate of 2 °C/min and then held at 110 °C for 4 hrs.

adopted drying method for Pond Sediment is reproducible and practically useful.

Both availability of apparatus and ease of operation were also taken into account in selecting a drying method, and finally oven-drying at 110℃ for 4 hrs was decided as the most convenient drying method for Pond Sediment.

As mentioned in Chapter I, however, for the determination of volatile elements such as Hg and Se, drying should be done on samples separate to those for analysis.

References

1) Iwata,Y., Okamoto,K., Matsumoto,K., Haraguchi,H. & Fuwa,K. (1979): *Abst. Joint U.S.-Japan Symposium on Standard Reference Materials* (Koriyama), p.8
2) Iwata,Y., Okamoto,K., Matsumoto,K., Haraguchi,H. & Fuwa,K. (1978): *Abst. Ann. Meeting Anal. Chem. Soc. Jpn.* (Kanazawa), p608
3) Okamoto,K. (1980): Preparation, Analysis and Certification of PEPPERBUSH Standard Reference Material, *NIES Res. Report No.18,* p.20-24
4) Iwata,Y., Okamoto,K., Matsumoto,K., Notsu,K., Haraguchi,H. & Fuwa,K.: *Bull. Chem. Soc. Jpn.,* submitted
5) Ando,A.(1975): *Bunseki*, 512
6) Tessier,A., Campbell,P.G.C. & Bisson,M. (1979): *Anal. Chem.*,51, 844
7) Davies,O.L. (1967): "Statistical Methods in Research and Production", Oliver and Boyd, London, p96; Ishikawa K., Fujimori T. & Kume H. (1967):"Jikken Keikaku-ho", Tokyo Kagaku Dojin, p202
8) Iwata,Y., Matsumoto,K., Haraguchi,H., Fuwa,K. & Okamoto,K.(1981): *Anal. Chem.*, 53, 1136

CHAPTER III

Analysis of the Surface Chemical Composition of Pond Sediment by X-Ray Photoelectron Spectroscopy

H. Seyama and M. Soma

1. Introduction

Pond Sediment, as prepared, can be regarded as a homogeneous ensemble of dried sediment particles of diverse chemical composition. Therefore, not only the inter-particle elemental distribution but also the intra-particle distribution of elements would be heterogeneous. Differences in the elemental composition between the surface layers and the bulk of the particle is an example of heterogeneity in the latter case. While the underlying general factor determining the distribution of elements between the surface and the bulk is a thermodynamic one, the difference might be due to the origin of the particle and/or the various chemodynamic events which the particle and its surface encountered in the environment. Such information characterizing the chemical nature of the sediment sample is of value when one uses Pond Sediment CRM as a standard in the analysis of a specific sediment sample and when one assesses the analytical data. The present work was intended to provide information about the surface chemical composition of Pond Sediment by applying X-ray photoelectron spectroscopy (XPS or ESCA)1), a modern analytical technique for surface analysis2) and one which has been considered to be most appropriate for chemical characterization of the surface of sediment particles.

XPS has a capability of identifying any element with inner shell electrons, that is, any element except hydrogen and helium. Its detection sensitivity primarily depends upon the photo-ionization cross section of inner shell electrons of the element of interest. For a given photon energy, the cross section for an element varies with subshell. However, if we consider the subshell of the largest ionization cross section for each element, the range of the detection sensitivity for elements is within a factor of about fifty3). This is the basis of XPS as an analytical tool for multi-element systems.

When an atom in a solid is ionized by soft X-rays, the mean free path of the ejected photoelectron in the solid matrix is not larger than several tenths of an angstrom4). Therefore XPS is surface sensitive, probing only several surface monolayers of a given solid sample. On the other hand the surface sensitivity of the XPS method, at the same time, severely limits its use as an analytical tool for analyzing the average bulk composition of the sample.

Finally, by measuring accurately the kinetic energy of the photoelectron emitted into vacuum, i.e. by determining the "chemical shift" in the core electron binding energy, one can get information on the chemical environment in which the element is embedded 1).

Because of the above-mentioned characteristics, XPS has been applied to a variety of scientific research problems. In the field of mineralogy and geochemistry, notably, chemical states of metallic ions in minerals, adsorption on the surface of minerals and dissolution from the surface have been studied successfully by XPS5). Considering the ability of XPS to determine multi-elements simultaneously, it is rather surprising to realise that applications to complex environmental samples have been confined so far to only a few examples such as aerosol particulates6).

2. *Outline of Elemental Analysis by XPS*

Figure 1 illustrates the two electron emission processes observed in actual XPS measurement, taking excitation of the sodium atom by magnesium Kα radiation as an example. In electron emission from the K shell, the kinetic energy, Ep, of the emitted photoelectron, e_p, is given by Eq.(1),

$$\mathrm{Ep} = h\nu - (\mathrm{BE})_K \qquad (1)$$

where $h\nu$ is the energy of the X-ray (1253.6 eV in this case) and $(\mathrm{BE})_k$ is the binding energy for the K shell electron. Measurement of the kinetic energy of the photoelectron determines the electron binding energy which can be assigned to a specific core electron of a specific atom, and hence the presence of a particular atom is assured. The electron emission from an inner shell leaves the atom in an unstable excited state and the atom immediately relaxes into a more stable state by releasing excess energy. An outer shell electron, say a L shell electron, makes a transition to the hole in the K shell releasing energy either by X-ray emission or by ejecting another outer shell electron into vacuum. The latter process is called an Auger transition and the one depicted in Fig.1 is a KLL Auger transition of sodium. The kinetic energy, $(\mathrm{KE})_A$, of the emitted electron, e_A, via the Auger process is given approximately by

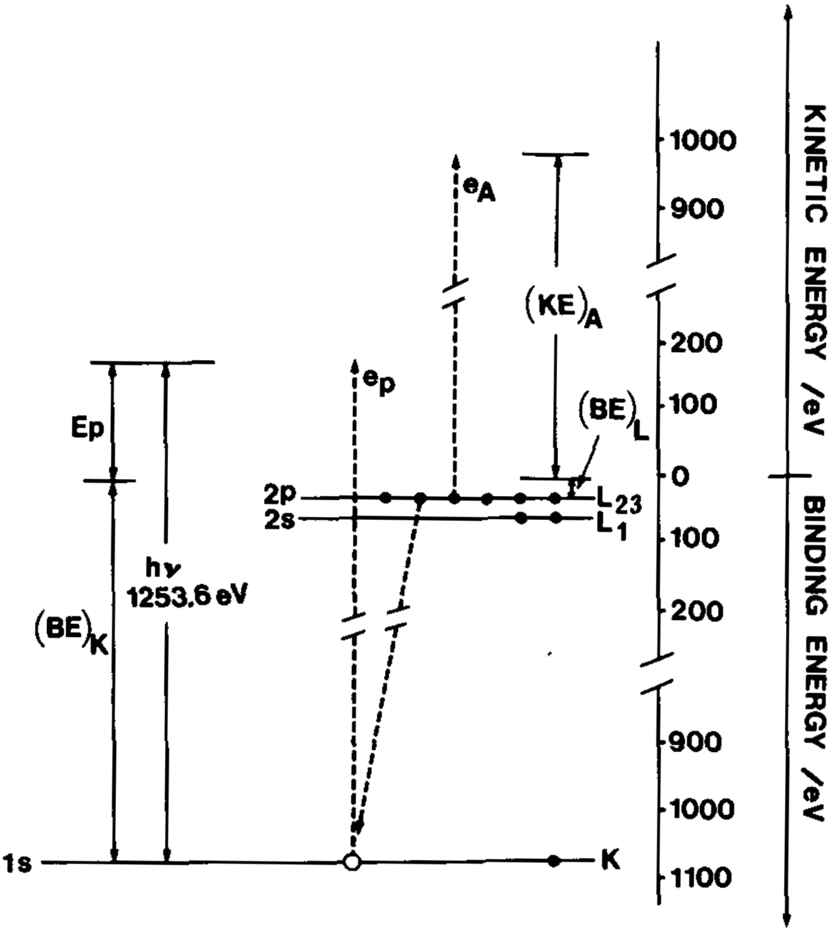
$$(\mathrm{KE})_A = (\mathrm{BE})_k - (\mathrm{BE})_L - (\mathrm{BE})_L \qquad (2)$$

, as is evident from Fig.1. Accordingly measurement of $(\mathrm{KE})_A$ identifies the relevant Auger transition and the atom responsible.

The measurement of the energy spectrum of both photo- and Auger electrons is the basis of identifying elements for qualitative elemental analysis by XPS (ESCA). An example will be seen in Fig.3.

Fig 1

Photoemission from K shell and KLL Auger electron emission from Na atom excited by Mg Kα radiation (1253.6 eV)



For quantitative analysis the relation between the intensity of the emitted electron and the relevant atomic concentration must be known. Let us consider photoelectron emission from a homogeneous solid sample containing the atom of interest with concentration N. The number of detected electrons per unit time emitted from the X shell of the atom is given by

$$I^X = \sigma^X(E_J)D(E^X)L^X(\gamma)\lambda(E^X)NJP \qquad (3)$$

provided that the configuration of the X-ray source, sample surface and the detector are fixed. In Eq. (3), J is the intensity of the incident X-ray; $\sigma^X(E_J)$ *is the ionization cross-section for shell X of the atom excited by a photon of* energy E_J; $\lambda(E^X)$ is the mean free path of the photoelectron with kinetic energy E^X in the solid; $L^X(\gamma)$ is the anisotropy of electron emission where γ is the angle between the incident X-ray and the detector; $D(E^X)$ is a constant *including the detection efficiency of the* analyzer and detector; P is the empirical peak factor which has been introduced to adjust the experimentally determined ionization cross section to the theoretical one$^{7)}$.

$\lambda(E^X)$ depends not only on E^X but also on the matrix in which the relevant atom is incorporated. However, for similar matrices, i. e. if the valence electron density per unit volume of the solid does not vary very much, λ can be regarded as a function of E^X alone. Therefore by measuring I^X's for reference materials of known atomic composition, one can get the relative atomic sensitivity, $I^X o$, taking the appropriate shell of a certain atom as a standard. For Auger electrons the emission intensities can be formally expressed as Eq. (3) and therefore the apparent atomic sensitivities for specific Auger transitions can be determined similarly.

Table I shows the relative atomic area intensities of some elements determined as their chlorides, fluorides and sulfates with an ESCA LAB 5, and demonstrates the feasibility of determining atomic sensitivities which are applicable to a range of compounds. In Table II, are included the relative atomic intensities of 2s and 2p subshells of Al and Si for halloysite and zeolites of known compositions.

To obtain $I^X o$ theoretically, the E^X dependencies of D, L, and λ must be known. $L^X(\gamma)$ is given by the following equation:

$$L^X(\gamma) = 1 + \frac{1}{2}\beta^X(\frac{3}{2}\sin^2\gamma - 1) \qquad (4)$$

where β^X has been theoretically calculated and tabulated$^{8)}$. For the ESCA LAB 5 electron spectrometer installed in NIES, γ is 65°. The dependence of $D(E^X)$ on E^X is determined by the characteristics of the electron energy analyzer. With the energy analyzer of ESCA LAB 5, when operated with a pass energy of 50V and an entrance slit width of 4 mm, D is inversely

Table I Atomic Intensities Relative to K 2p

Element	Line	Chloride	Fluoride	Sulfate
		Excited by Mg Kα		
Na	1s	0.873	1.05	
	2s	0.106	0.090	
	$KL_{23}L_{23}$Auger		1.35	
Mg	2s	0.162	0.133	
K	2s	0.317	0.314	0.308
Ca	2s	0.298	0.301	
	2p	1.18	1.13	
Al	2s		0.170	0.162
	2p		0.161	0.149
		Excited by Al Kα		
Na	1s	1.19	1.30	
	2s	0.109	0.106	
	$KL_{23}L_{23}$Auger	1.26	1.32	
Mg	2s	0.183	0.151	
	$KL_{23}L_{23}$Auger	2.16	1.90	
K	2s	0.405	0.398	
Ca	2s	0.375	0.399	0.392
	2p	1.17	1.19	
Al	2s		0.189	0.190
	2p		0.114	0.132

Table II Relative Atomic Intensities for Al and Si[a]

Line		Halloysite[b] $Al_4Si_4O_{10}$ $(OH)_8 \cdot 4H_2O$	Zeolite 4A $Na_2O \cdot Al_2O_3$ $SiO_2 \cdot 6H_2O$	Zeolite 13X $0.9Na_2O \cdot Al_2O_3$ $2.5SiO_2 \cdot 8H_2O$
		Excited by Mg Kα		
Al	2p	1	1	1
Al	2s	1.12	1.15	1.19
Si	2p	1.71	1.62	1.70
Si	2s	1.36	1.33	1.36
		Excited by Al Kα		
Al	2p	1	1	1
Al	2s	1.68	1.45	1.62
Si	2p	1.88	1.90	1.80
Si	2s	2.00	1.88	1.89

a: Relative to Al 2p line.

b: A.P.I. clay from Eureka, Utah, USA.

proportional to the square root of E^x[7) for normal operating conditions. On the other hand λ is approximately proportional to the square root of E^x. Therefore, I^x is approximated by

$$I^x \propto \sigma^x(E_J)L^x(\gamma)NP \qquad (5)$$

Thus the relative atomic sensitivity for the specific shell can be determined experimentally or calculated by Eq. (5). The theoretical estimate is convenient in the case when, for the element of interest, a material of specified quality with a definite composition is not at hand.

The relative sensitivity for the atoms obtained by the above procedures is tabulated in Table III, where Al 2p is used as a standard. The experimentally determined sensitivity was obtained from measurements of the area of the respective peaks for compounds of known purity as shown in Table I. For Si, the peak intensity relative to Al 2p was determined from Table II. With this, the Si/Al ratios for NBS Standard Reference Materials, 97a (flint clay) and 98a (plastic clay), agreed to within 10 % of the certified values.

Table III

Relative Atomic Sensitivity of the Elements (Al 2p=1)

Element	Line	Al Kα	Mg Kα
Al	2s	1.58	1.15
Si	2p	1.86	1.67
Si	2s	1.92	1.35
Fe	2p	19.7	14.8
Fe	3p	1.91	1.51
Ca	2p	8.93	7.76
Ti	2p	9.23[a]	8.03[a]
Mg	$KL_{23}L_{23}$Auger	15.4	—
Na	$KL_{23}L_{23}$Auger	9.77	9.03
O	1s	3.52[b]	2.95[b]
C	1s	1.36[b]	1.17[b]
N	1s	2.39[b]	2.03[b]
P	2p	2.21[b]	2.02[b]

a: Theoretical estimations based on the procedures described in the text.

b: Theoretical estimations, but also substantiated by the experimental measurements of reference materials not belonging to the group in Table I and II.

3. *Experimental*

A. Apparatus

The electron spectra were recorded on a Vacuum Generator ESCA LAB 5 apparatus. The apparatus is essentially a composite electron- and mass spectroscopic surface analytical system with several excitation sources. A schematic diagram of the apparatus and the flow of the measurement relevant to XPS are shown in Fig.2. The surface of a solid sample, placed in the center of the analyzer chamber, is excited by Al Kα or Mg Kα radiation from a twin anode and the emitted photoelectrons are transferred to a 150° hemispherical electron energy analyzer through a transfer lens situated at an angle of 65° from the direction of the incident X-rays. The electron kinetic energy is retarded to a constant pass energy for the analyzer by a mesh electrode placed at the entrance of analyzer and the analyzer acts as a filter with a very narrow band pass. The electrons which pass through the analyzer are then detected by a channel electron multiplier.

In the measurement of Pond Sediment, the following conditions were chosen: X-ray power, 13 kV × 10 mA; electron pass energy, 50V; width of the entrance slit, 4 mm.

B. Procedures

Pond Sediment powder was placed onto double-sided adhesive tape fixed on a stainless steel sample holder of 10 mm diameter. The base pressure of the chamber rose from 10^{-10} Torr to about 10^{-8} Torr during the measurement. To determine the intensity of weak transitions, signals for narrow range scans (12.5-50 eV) were accumulated on a Nicolet 1070 signal averager until appropriate signal to noise ratios were attained. For many elements, photoemission intensities were stable during long-time exposure to X-rays. However, the intensities of C 1s and N 1s lines changed significantly during the measurement at room temperature. This instability was suppressed to a negligible level when the sample was cooled by a continuous flow of liquid nitrogen through the specimen manipulator. The quantification of the element was based on the integrated intensity of the emission line. The binding energies were calibrated against the Au $4f_{7/2}$ line for gold film which was evaporated onto the sample and which was taken to be 83.8 eV. The uncertainty in the binding energy determination was ± 0.2 eV.

4. *Results and Discussion*

A. The Surface Elemental Composition of Pond Sediment

Figure 3 exemplifies a wide scan spectrum of Pond Sediment excited by Al Kα radiation. Assignments for major peaks are indicated in the figure and such a wide scan is capable of identifying major elements in Pond Sediment. The KLL Auger transitions of Mg and Na are intense enough that the Auger peaks were detectable in spite of their relatively low concentrations (see Table IV).

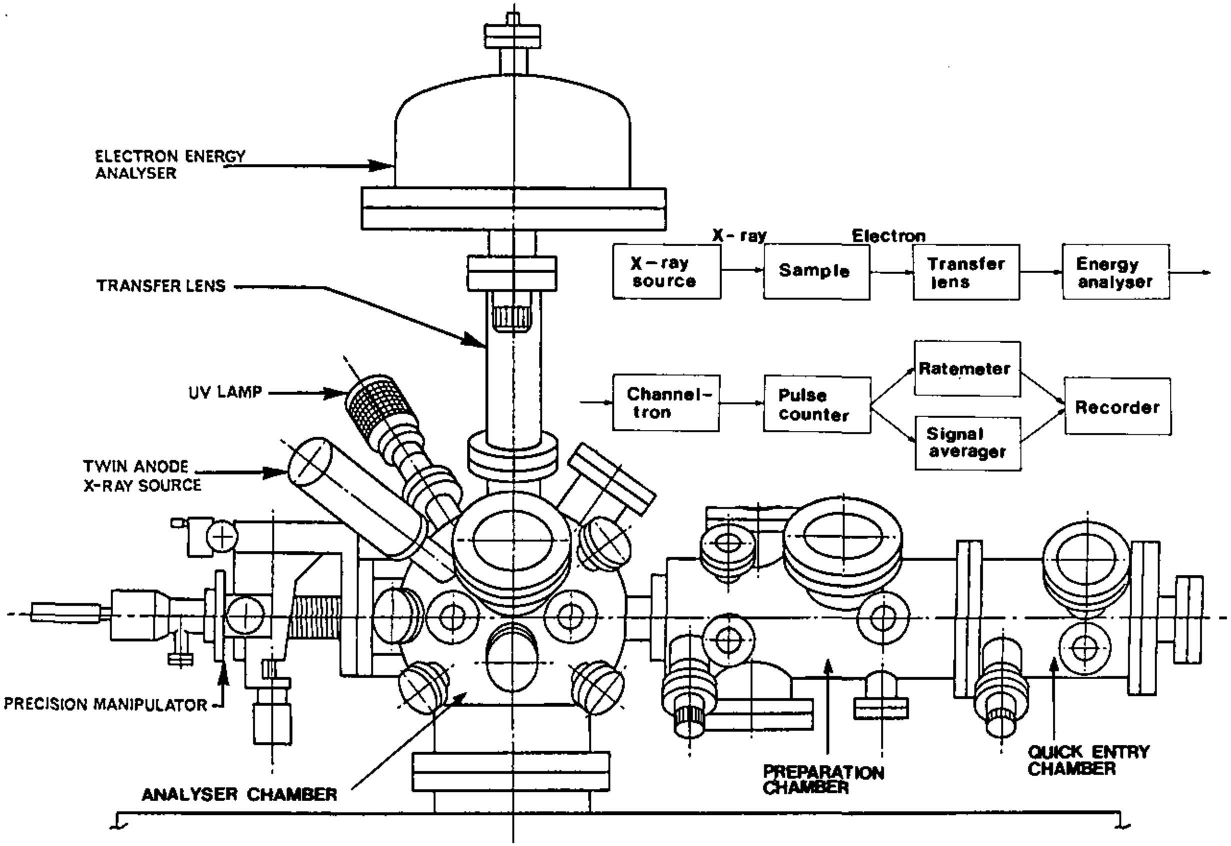


Fig 2. Schematic diagram of ESCA LAB 5 apparatus and flow of measurement.

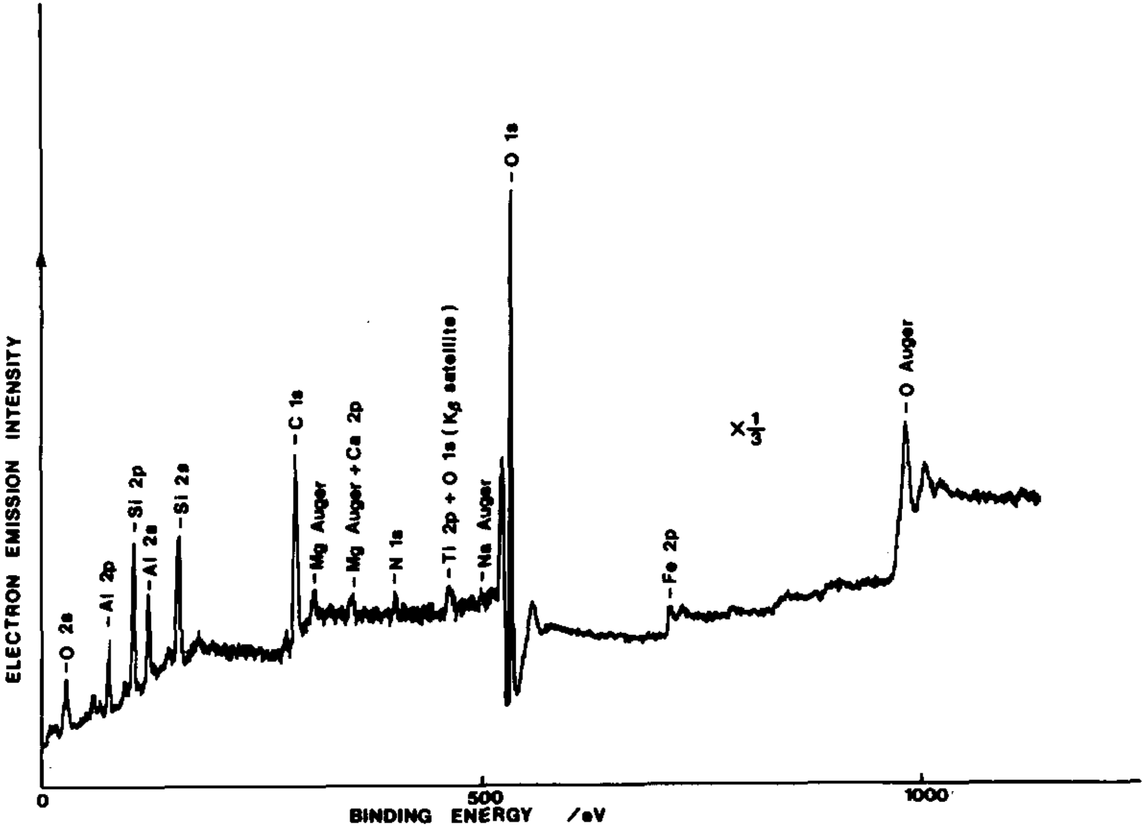


Fig 3. A wide scan spectrum of Pond Sediment excited by Al Kα radiation.

The area intensities of the relevant lines of several elements were determined relative to that of the Al 2p line and are summarized in the 4th column of Table IV. From the intensity ratios and the atomic sensitivities given in Table III, the relative atomic composition of the elements were estimated. The 5th and 6th columns of Table IV include the estimated atomic compositions based on Al 2p and Si 2s, respectively. They can be compared with the corresponding bulk compostions (by chemical analysis) compiled in the 7th and 8th columns respectively. The choice of the standard element is quite arbitrary but the inspection of the results suggests that the use of XPS intensity of Si 2s as the standard appears to be more appropriate than that of Al 2p. The concentration of Al in the surface layers as determined by XPS is different from that of the bulk composition, being apparently surface enriched. Differences between the surface and bulk concentrations of individual particles result in differences in elemental composition determined by XPS as compared to the data for bulk analysis. Besides, large discrepancies in the size distributions of particles of different elemental composition could also cause the apparent surface composition to deviate from the bulk one, if, for example, smaller particles are attached on the surface of larger ones to form loose composite particles. Since informations concerning such marked heterogeneity in the particle size distribution are not available for Pond Sediment, we tentatively attributed the observed difference between XPS and bulk analysis to the different elemental distributions in the surface layers of individual particles.

Table V shows the atomic concentration of O, C, N and P relative to Si determined from measurements on two chilled samples. Notably, the XPS concentrations of nitrogen and carbon were about four times as large as the bulk concentrations. As will be described below, most nitrogen and carbon originate from organic matter. The C to N ratio of 16.4 obtained by XPS is close to the ratio of 14.8 for the bulk composition. Accordingly the contribution from contaminating C which is always found on solid samples is comparatively small. The results did demonstrate the accumulation of organic matter on the surface of the particles. Phosphorus was quantified by the most intense 2p line. However, the low abundance of P and the overlap with the onset of the broad loss peak of Al 2s hindered accurate measurement of the line intensity. An estimation indicated the concentration of P relative to Si was higher in the surface layers.

The other elements included in Table IV did not show such a high surface concentration as C and N. The surface abundance relative to Si was higher than the bulk one with Al and Fe, not much different with Ca and Ti, and smaller with Mg and Na. The difference in Mg concentration may not be significant, but the difference in Fe was considered to be real as will be discussed below.

Table IV

Atomic Composition Determined by XPS

				Atomic Composition			
Element	Line	Source	Relative[a] intensity	XPS		Bulk Composition[c]	
			Al 2p=1	Al 2p=1	Si 2s=1	Al=1	Si=1
Al	2p	Al	1	1	0.83	1	0.53
		Mg	1	1	0.82		
	2s	Al	1.54(7)	0.98(4)	0.81		
		Mg	1.15(4)	1.00(3)	0.82		
Si	2p	Al	2.25(2)	1.21(1)	1.00	1.90	1
		Mg	2.02(8)	1.21(5)	0.99		
	2s	Al	2.31(1)	1.21(1)	1		
		Mg	1.65(5)	1.22(4)	1		
Fe	2p	Al	6.09(13)	0.31(1)	0.26	0.30	0.16
	3p	Al	0.48(1)	0.25(1)[b]	0.21[b]		
Ca	2p	Mg	0.23(1)	0.030(1)	0.026	0.052	0.027
Ti	2p	Mg	0.16(1)	0.020(1)	0.017	0.034	0.018
Mg	$KL_{23}L_{23}$Auger	Al	0.55(5)	0.036(2)	0.030	0.097	0.051
Na	$KL_{23}L_{23}$Auger	Al	0.12(1)	0.013(1)	0.010	0.063	0.033

a: Average for 3 samples. Numbers in parenthesis represent probable errors in the last figure.

b: Average for 2 samples.

c: See chapter VII of this report.

Table V

Surface Abundance of O, C, N and P

Element	Line	Atomic composition (Si=1) XPS[a]	Bulk composition
O	1s	6.3 ±0.3	
C	1s	2.46±0.08	0.59
N	1s	0.15±0.015	0.040
P	2p	0.01±0.001	0.0059

a: Determined by the duplicate measurements of the area intensity for the chilled sample.

The distribution of an element between the bulk and surface should be affected by the origin of the sediment particles and by the history of the particles before and after they were introduced in aquatic systems. For instance, a liquid-surface partitioning is considered to be important in determining the surface Fe concentration. Actually this partitioning has been shown for a sediment from Lake Kasumigaura; the samples freeze-dried immediately on collection had the surface Fe concentration about 30 % higher than the samples freeze-dried after most of the water was removed by centrifugation. This observation indicates that the deposition of Fe from the aqueous phase onto the surface of sediment particles contributes considerably to the surface concentration. Also a photoelectron emitted from the Fe 2p orbital has a smaller kinetic energy than one from the Fe 3p orbital, and hence has a smaller escaping depth from the solid.4) Therefore, the larger surface Fe concentration deduced from the Fe 2p line than from the Fe 3p line also supports the surface enrichment of Fe.

Na is apparently depleted in the surface in contrast to the smaller difference in the surface Mg concentration from the bulk concentration. As shown in Fig 4, the K 2p intensity was very weak relative to the Ca 2p line, although accurate intensity measurement of the K 2p was impossible due to spectral interference by the intense C 1s line. Since the XPS sensitivities for the 2p line and the bulk concentration of K and Ca (see chapter VII of this report) are roughly the same, the result indicates that the surface concentration of K is much smaller than that of Ca, an alkaline earth element in the same period, as is the case of Na versus Mg. Whether the depletion of Na and

K was caused by the leaching of these ions from the surface is not certain at the present stage of the investigation. The depletion may also be caused by the original surface composition when the particle was formed. A similar depletion effect was also found for a finely powdered rock sample which showed a surface composition significantly different from the bulk composition.[9)]

Finally, let us briefly discuss the amount of oxygen. If we assume the stoichiometry of the respective oxides for the elements in Table IV and of the carbohydrate for carbon, the relative abundance of O against Si is calculated to be 6.15 which is very close to the observed value of 6.3. The oxide stoichiometry tends to underestimate the amount of O bound to the metallic elements because of the existence of surface hydroxyls, while the carbohydrate stoichiometry tends to overestimate the amount of organic O because humic substances have less oxygen than carbohydrates. Both the excess and deficient amounts can account for as much as 50 % of the stoichiometric compositions. However, as both effects cancel each other, the reasonable agreement between the calculated and observed values supports the overall validity of the present analytical procedures.

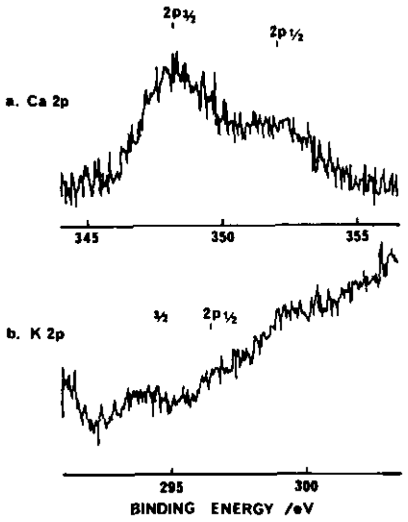


Fig 4. Spectra of Ca 2p (a) and K 2p (b) regions of Pond Sediment

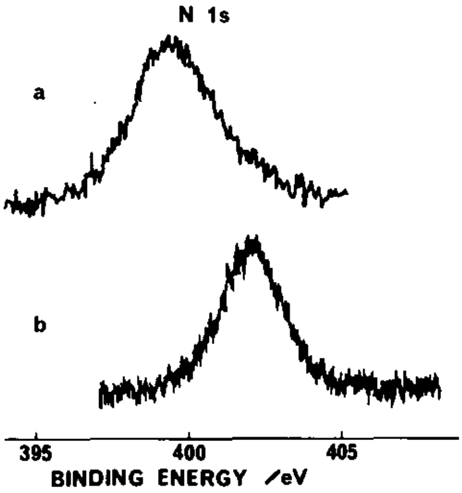


Fig 5. N 1s spectra of Pond Sediment (a) and NH_4^+–montmorillonite (b)

Table VI

Binding Energies of Photoelectrons and Kinetic Energies of Auger Electrons

Emission line		Electron Energy (eV)	
		Pond Sediment	Compounds[a]
O	1s	531.9	531.2 (α-Al_2O_3) 532.6 (SiO_2 gel)
Al	2p	74.3	73.6 (α-Al_2O_3) 74.3 (montmorillonite)
Al	2s	119.3	119.1 (α-Al_2O_3) 119.0 (montmorillonite)
Si	2p	102.5	103.2 (SiO_2 gel) 102.4 (montmorillonite)
Si	2s	153.6	153.4 (montmorillonite)
Fe	2p3/2	711.2	710.8 (α-Fe_2O_3)[b] 711.3 (γ-FeOOH)[b]
N	1s	399.3	
Mg	$KL_{23}L_{23}$Auger	1180.3	1180.0 ($MgCl_2 \cdot 6H_2O$) 1180.7 (MgO) 1181.2 (montmorillonite, non-exchangeable Mg) 1179.2 (montmorillonite, exchangeable Mg)
Na	$KL_{23}L_{23}$Auger	988.8	988.6 (NaF) 988.7 (Na-montmorillonite)
P	2p	133.3	133.4 ($NaH_2PO_4 \cdot 2H_2O$)
Ca	2p3/2	347.8	346.3 (CaO)[c], 348.6 ($Ca(OH)_2$)[c] 346.6 ($CaCO_3$)
Ti	2p3/2	458.5	458.6 (TiO_2)[d]
C	1s	284.7	

a: Au 4f7/2=83.8 eV or C 1s=284.4 eV (for carbon contamination) approximately compatible with the Au 4f value in most cases was taken as a reference.

b: H.Konno and M.Nagayama, J.Electron Spectrosc. 18, 341 (1980)

c: Y.Inoue and I.Yasumori, Bull, Chem Soc, Japan, 54, 1505 (1981)
C 1s level of contaminating carbon, 285.0 eV, was taken as a reference.

d: L.T.Anderson, J.C.S.Faraday I, 75, 1356 (1979); C 1s=284.3 eV

B. The Electron Binding Energies

Table VI summarizes the binding energies (kinetic energies for Auger transitions) of the main photoemission peaks of the respective elements. Included in the table are the binding energies for the relevant compounds. It is evident that each element in the sediment is present in the expected valence state. However, more accurate determination of the binding energies and the comparison with a larger number of reference compounds are necessary to define the chemical states of the elements in more detail. Figure 5 compares the N 1s spectrum of Pond Sediment with that of ammonium ion adsorbed on montmorillonite. The binding energy of N in Pond Sediment is lower by about 2.1 eV, demonstrating that nitrogen in the sediment is mostly of organic origin such as amine etc. The C 1s peak which appeared at 284.7 eV is a value typical for skeletal carbon of organic compounds. Accordingly the main part of carbon also originates from organic substances in the sediment.

5. *Conclusion*

The present study has demonstrated a considerable deviation of the surface elemental composition from that of the bulk composition of Pond Sediment and, at the same time, has demonstrated the ability of XPS (ESCA) in characterizing the surface chemical composition of sediment samples. To clarify how these surface characteristics are related to the origin and history of the sediment, further works are required. Such works would certainly be worth-while.

References and Notes

1) ESCA is the abbreviation for Electron Spectroscopy for Chemical Analysis, introduced by K. Siegbahn and his co-workers in their now classical book; K. Siegbahn *et al.*, (1967): "ESCA", Almqvist and Wiksells, Uppsala.
2) Czanderna,A.W. (ed) (1975):"Methods of Surface Analysis",Elsevier, Amsterdam.
3) Scofield,J.H. (1976): *J. Electron Spectrosc.*, 8, 129
Evans S., Pritchard R.G. & Thomas J.M. (1978): *ibid*, 14, 341
4) Palmberg,P.W. (1973): *Anal. Chem,* 45, 549A
Powell,C.J. (1974): *Surface Sci.*, 44, 29
Brundle,C.R. (1974): *J. Vac. Sci. Technol.*, 11, 212
5) Bancroft,G.M., Brown,J.R. & Fyfe,W. S. (1979): *Chem. Geol.*, 25, 227
6) See for example, Lindfors P.A. & Hovland C.T. in T.Y. Toribara *et al* (ed) (1978): "Environmental Pollutants", p349, Plemum, New York
7) Seah,M.P. (1980): *Sunf. Interface Anal.*, 2, 222
8) Reilman,R.T., Msezane,A. & Manson,S.T. (1976): *J. Electron Spectrosc.*, 8, 389
9) This was found for the basalt powder prepared by Geological Survey of Japan as a geochemical standard, JB-1.

CHAPTER IV

Analysis of Pond Sediment by Atomic Absorption Spectrometry

K. Okamoto

1. Introduction

In recent years atomic absorption spectrometry (AAS) has become one of the most popular analytical techniques for the determination of metallic elements in diverse samples. The acceptance of AAS is attributed mainly to the following factors: (1) high specificity, (2) high sensitivity, (3) ability to control and overcome matrix interference, if present, and (4) rapid analysis utilizing relatively simple and easy-to-operate instrumentation.

The atomic absorption technique can be grouped into categories: (a) flame AAS, (b) non-flame AAS, with respect to the mode of producing the atomic vapour. Historically, a flame has been the means of atomization for AAS and is still the basic source for the vast majority of AAS measurements, because of the advantages indicated above. However, disadvantages are that a relatively large quantity of sample is required and sensitivity is limited for many elements.

A relatively new technique for producing the atomic vapour is the non-flame devices. These devices can be grouped into categories such as (a) the cathodic sputtering technique, (b) graphite furnace or carborn rod devices, (c) tantalum ribbon and (d) the cold vapour method. These methods differ from flames in that the atomization source is more conducive to the production of ground state atoms in contrast to the chemically reactive flame environment. Also, for the graphite furnace or carbon rod only a relatively small volume of the sample (1 to 50 μl) is necessary for analysis which gives these methods improved sensitivity over flame methods. However, the non-flame methods have the inherent disadvantage in that high precision is more difficult to attain1).

One of the more recent developments in the field of atomic absorption is the use of metal-hydride generation systems for the determination of volatile elements such as As and Se. The metal-hydride generated by mixing a reducing agent with an appropriate acid is introduced to a hydrogen-argon flame or quartz absorption cell where the metal-hydride is dissociated into the free atom. This technique is relatively free from interference, however, it is rather difficult to select the best conditions for generating the metal-hydride. There have been a number of reports on metal-hydride generation systems because the elements suitable for this technique are of biological and environmental interest$^{2\text{-}6)}$. The sequential separation and determination of various As or Se compounds by this technique have also been carried out varying the concentrations of both reducing reagent and acid$^{7\text{-}11)}$.

Before describing the analysis of Pond Sediment by AAS, some characteristics of sediments are given and their dissolution procedures are reviewed.

Sediments, substantially heterogeneous, consist of both inorganic and organic material, so that their complex composition may often inhibit accurate determination of heavy metals. For example, typical sediment samples contain 5-10 percent of Al and Fe as matrix elements, while the concentrations of heavy metals of environmental concern are usually less than 100 μg/g. The accurate determiantion of trace elements in the presence of such complex matrices may require, therefore, appropriate sample pretreatment. AAS tends to suffer from chemical interferences, so that procedures to remove interfering elements are very often required. The separation of the elements to be measured from matrix constituents using solvent extraction technique has been mostly employed to minimize interferences by major elements$^{12\text{-}14)}$.

The presence of organic matter in sample solution may also prevent the accurate determination of heavy metals. Generally, sediments contain relatively high amounts of organic matter, and normally, the complete destruction of organic matter is necessary to achieve meaningful AAS measurement. For sample dissolution, the addition of perchloric acid as well as nitric and hydrofluoric acids has been widely employed. For the determination of non-volatile elements, dry-ashing of the sample before dissolution may be effective to remove organic material.

Certain elements such as Hg and Se are volatile and may exist, in part, in the sediment in an organic form which is usually more readily vapourized than the inorganic forms. Thus, for the determination of such volatile elements special attention must be paid to the procedures of drying and dissolution in order to retain the elements.

Sample preparation depends on the type of sediments, the elements to be measured and the precision and accuracy required. For elemental analysis, standard alkali fusion or acid decomposition using hydrofluoric acid has been employed in order to dissolve the sediments. This approach enables results to be expressed on a total basis, a prime requirement in the CRM field. The extraction of elements from sediments using an appropriate extractant has also been performed in fields related to plant nutrition and soil chemistry. In analyzing Pond Sediment by AAS, complete dissolution of samples was carried out using a mixture of nitric, hydrofluoric and perchloric acids and all analytical values are given on a total basis.

2. *Sample Preparation*

a. Dissolution of Pond Sediment

About one gram of Pond Sediment was dried in a glass weighing bottle at 110℃ for 4 hrs in an oven. The mean moisture loss of 9 samples was 11.12 percent for the above conditions. The dried sample was transferred to a Teflon beaker (100 ml) and 20 ml of nitric acid (1:1) was added. After heating on a hot plate (200℃) for one hour, 5 ml of nitric acid and 15 ml of hydrofluoric acid were added and the mixture was evaporated to approximately 10 ml. After cooling, the insides of the beaker were rinsed with distilled water and 10 ml of perchloric acid was added. Then the sample was heated (200℃) until the appearance of white fumes. Subsequently, hydrofluoric acid (10 ml) and perchloric acid (10 ml) were added again in order to remove silica and to destroy organic matter completely, and the mixture was heated to reduce the sample volume to approximately 5 ml. Finally, 20 ml of distilled water was added and the solution was filtered through an acid-washed filter paper (Toyo 5A). The filter paper was washed with a small volume of 0.1 M perchloric acid and the sample solution volume was adjusted to 100 ml with distilled water. The digested sample solutions were subjected to flame AAS measurement.

b. Solvent extraction

In order to eliminate interferences by matrix elements, the use of solvent extraction has very often been employed. At the same time preconcentration of the desired metals can be attained using this technique. In the case of sediment analysis, Fe and Al are the interfering elements in many cases. Therefore, extraction conditions whereby the interfering and the desired elements can be completely separated into aqueous and organic phases respectively must be decided. A variety of solvent extraction techniques have been applied with varying chelating reagents, solvents and pH. In this experiment sodium diethyldithiocarbamate (DDTC) and methylisobutylketone (MIBK) extraction system, which is the official method for the analysis of sediments by the Environmental Agency of Japan15), was used for the simultaneous extraction of Pb, Cu, Zn, Cd, Ni and Co.

100 ml of the sample solution (1 g to 100 ml), prepared as mentioned above, was transferred to a 200 ml beaker and 20 ml of 50 % ammonium citrate (AAS grade) was added to it. The pH of the solution was adjusted to 9.5 by the addition of ammonium hydroxide (AAS grade) and the solution was then transferred into a 300 ml PTFE separating funnel. After the addition of 20 ml of 1 % DDTC (AAS grade) and 20 ml of MIBK (AAS grade)

into the separating funnel, the mixture was vigorously shaken on a mechanical shaker for 2 min and then the phases were allowed to separate over a 10 min period. After draining off the aqueous layer into a 200 ml beaker, the MIBK layer was transferred into a 100 ml beaker. A further 10 ml of MIBK was added again to the aqueous layer and the mixture was shaken for 2 min and allowed to stand for 10 min. The two MIBK extracts were combined in the 100 ml beaker and heated gently on a hot plate to dryness. Approximately 10 ml of nitric acid (1:1) was added to the resultant residue and the solution was heated to near dryness. Next 5 ml of nitric acid was added and the resultant solution was quantitatively transferred into a small Teflon beaker (25 ml).The beaker was heated to reduce the nitric acid solution to approximately 0.5 ml. The insides of the beaker were rinsed with a small volume of distilled water, and the solution was quantitatively transferred into a 10 ml volumetric flask and filled to the mark with distilled water. Consequently, a 10-fold preconcentration of the heavy metals was achieved.

c. Nitric and sulfuric acid dissolution for determination of As

For the determination of As in Pond Sediment, the following sample dissolution procedure was employed[15]. Approximately one gram of Pond Sediment was taken in a 200 ml conical beaker, and distilled water, nitric acid and sulfuric acid (10 ml, each) were added. The beaker, covered with a watch glass, was heated on a hot plate at 250 ℃ and evaporation of the sample solution was continued to approximately 5 ml. After cooling and rinsing the insides of the beaker with distilled water, 10 ml of nitric acid was added and heated until the appearance of white humes of sulfuric acid. This procedure was repeated twice to achieve complete digestion of the sample and to expel nitric acid from the sample solution. After rinsing the insides of the beaker with a small volume of distilled water, the solution was filtered (Toyo 5B) and made up to 100 ml with distilled water. This sample solution was employed for the determination of As using the As-hydride generation technique.

3. Determination of metals in Pond Sediment

The determination of metals in Pond Sediment was carried out by AAS using an air-acetylene flame. Standard stock solutions (1000 ppm of each element) were prepared either by dissolving high purity metal powders in appropriate acids or by dissolving high purity metal-salts in distilled water, as described in the previous report[16]. A series of individual standard working solutions were prepared by appropriate dilutions of the 1000 ppm stock solutions with 0.1 M perchloric acid. For the determination of Pb, 0.1 M nitric acid was used for diluting the 1000 ppm stock solution. The ranges of the standard working solution were chosen to encompass the concentrations in the Pond Sediment solution.

The calibration curve method was used for the determination of metals and at the same time the standard addition method was also employed for certain elements which were expected to suffer from matrix interference. Table I summarizes the analytical conditions used for the determination of each element.

Table I

Experimental Conditions for Determinations of Elements in Pond Sediment by AAS

Element	Analytical Line (nm)	Lamp Current (mA)	Slit Width (Å)	Flow Rate Air-Acetylene (1/min)	Burner Height (mm)	Background Correction (D_2 Lamp)
Fe	248.3	9	1.9	10-2.5	4	Yes
Mg	285.2	5	3.8	10-2.5	5	Yes
Ca	422.7	8	3.8	10-2.6	8	No
K	769.9	7	3.8	10-2.5	5	No
Na	589.6	6	3.8	10-2.5	4	No
Mn	279.5	5	1.9	10-2.5	4	Yes
Zn	213.8	6	3.8	10-2.5	4	Yes
Cu	324.8	7	3.8	10-2.3	5	No
Pb	283.3	7	3.8	10-2.6	4	Yes
Cr	357.9	5	3.8	10-3.3	8	No
Rb	780.0	8	3.8	10-2.5	4	No
Ni	232.0	9	1.9	10-2.5	4	Yes
Co	240.7	9	1.9	10-2.4	4	Yes
Cd	228.8	5	3.8	10-2.3	4	Yes

Spectrometer :	Shimazu AA-640-12 atomic absorption and flame emission spectrophotometer
Lamp :	Hollow cathode lamp (HamamatsuTV)
Flame :	Air-acetylene flame

The analytical values for each element are given in Table II. For the determinations of Fe, Mg, Ca, K, and Na the sample solution (1 g to 100 ml) was diluted 100 times with 0.1 M perchloric acid.

In the case of Ca and Mg, serious chemical interference was observed, so that two approaches, the standard addition method and the addition of lanthanum to the standards and samples, were applied to correct for the interferences. For example, when the calibration curve method was adoped a Ca value two orders of magnitude lower than expected was obtained. This low result is explained by removal of the free gaseous Ca atoms by formation of a Ca-Al complex which, in the relatively low temperature air-acetylene flame, is hard to dissociate. In order to overcome such chemical interference problems, the addition of lanthanum to sample solutions has been routinely applied to determine Ca and the standard addition method has also been used as an alternative approach. The use of a high temperature flame such as the nitrous oxide-acetylene flame is also effective for dissociating the Ca-Al complex into free Ca atoms. In the case of Pond Sediment analysis, the addition of lanthanum chloride to the sample solution (final La concentration: 5000 ppm) gave consistent values for Ca when both the calibration curve and standard addition methods were used. On the contrary, in the absence of lanthanum the standard addition method did not yield consistent results. These findings were also observed for Mg determination.

The three different procedures, calibration curve, standard addition and solvent extraction, were used for the determinations of Zn, Cu, Pb, Ni, and Co in Pond Sediment. The analytical values for these elements by the three procedures, as shown in Table II, were consistent, though small biases may be noted. The analytical values for the elements are within the uncertainties of the certified values for each element.

Cadmium in the sample solution (1 g to 100 ml) exists at the ng/ml level so that it was not possible to directly determine Cd using flame AAS. The use of graphite furnace AA was also not successful, because of severe matrix interference by Al and Fe. Therefore, the separation and concentration of Cd by solvent extraction was required for the determination of Cd in Pond Sediment. The analytical value for Cd obtained by solvent extraction-flame AAS was very close to that by isotope-dilution mass spectrometry.

In the analysis of chromium, the value obtained by AAS was lower than that by alkali fusion-colorimetry determination using diphenylcarbazide. The loss of Cr during acid digestion has been demonstrated in many works, therefore, alkali fusion of sediment samples is desirable for the sample pretreatment of Cr analysis.

Arsenic in Pond Sediment was determined by AAS using the hydride -generation technique. The sample solution prepared by sulfuric-nitric acid digestion was mixed with sodium borohydrate and hydrochloric acid, and then the resultant arsine was introduced to a quartz tube (10 cm) heated at approximately 1,000 ℃. Arsine was dissociated into As atoms within the tube where atomic absorption measurements were performed. The standard addition method was used for the determination of As in Pond Sediment. The analytical value for As will be discussed in Chapter VII.

Mercury in Pond Sediment was determined by the Ag-trap cold vapour technique and with a Zeeman-effect mercury analyzer. The mercury content of Pond Sediment is relatively high so that approximately 50 mg of the sample was subjected to AAS analysis. The analytical values for mercury by the two methods were consistent.

Table II

Analytical Results for Pond Sediment by AAS

Element	Analytical values by			certified or reference values
	calibration curve	standard addition	solvent extraction	
Fe(wt.%)	6.43	–	–	6.53±0.35
Mg	0.550 0.963 1)	0.785 0.951 1)	–	–
Ca	0.838 1)	0.852 1)	–	0.81±0.06
K	0.678	–	(0.692) 4)	0.68±0.06
Na	0.534	–	(0.562) 4)	0.57±0.04
Mn(μg/g)	774	768	–	(770)
Zn	343	354	338	343±17
Cu	210	220	223	210±12
Pb	107	105	110	105±6
Cr	62.4	68.5	–	75±5
Rb	–	43.9	(43.4) 4)	(42)
Ni	35.8	34.6	41.7	40±3
Co	29.4	29.9	24.1	27±3
Cd	–	–	0.827	0.82±0.06
As	–	11.5	–	12±2
Hg	1.42 2) 1.38 3)	–	–	(1.3)

1) La added (5000 μg/ml).
2) Ag-trap cold vapor AAS
3) Zeeman AAS
4) determined by flame emission spectrometry

References

1) Rains,T.C. (1974): *Special Technical Publication* 564, American Society for Testing and Materials, p. 50-67
2) Agemian,H. & Thomson,R. (1980): *Analyst,* 105, 902
3) Verlinden,M., Baart,J. & Deelstra,H. (1980): *Talanta,* 27, 633
4) Brooke,P.J. & Evans,W.H. (1981): *Analyst,* 106, 514
5) Korenaga,T. (1981): *Analyst,* 106, 40
6) Paolo,S.G. & Calro,G. (1981): *Talanta,* 28, 169
7) Howard,A.G. & Arbab-Zavar (1981): *Analyst,*106, 213
8) Andreae,M.O., Asmode,J.F., Foster,P. & Vantdack,L. (1981): *Anal. Chem.,* 53, 1766
9) Yamamoto,M., Urata,K. & Yamamoto,Y. (1981): *Anal. Lett. part A,* 14, 21
10) Hinners,T. A. (1980): *Analyst,* 105, 751
11) Hahn,M.H.,Mulligam,K.J., Jackson,M.E. & Caruso,J.A. (1980): *Anal. Chim. Acta,* 118, 115
12) Pedersen,B., Willems,M. & Jorgensen,S.S. (1980): *Analyst,* 105, 119
13) Sanzolone,R.F. & Chao,T.T. (1981): *Analyst,* 106, 647
14) Clark,J.R. & Viet,J.G. (1981): *Anal. Chem.,*53, 61
15) Environment Agency of Japan (1975): *Teishitsu Chosa Ho* (in Japanese)
16) Okamoto,K. (1980): *Preparation, Analysis and Certification of PEPPERBUSH Standard Reference Material,* NIES Research Report No.18, p.25-32

CHAPTER V

Analysis of Pond Sediment by Inductively Coupled Plasma Atomic Emission Spectrometry

K. Okamoto, M. Nishikawa and C.W. McLeod

1. Introduction

Trace element determinations in a large number of sediments have been carried out for environmental impact studies. However, the complexity of the sample matrix and the low levels at which many elements of environmental interest occur makes elemental analyses of sediments a difficult task. In most cases, trace element analyses of sediments have involved some type of mineral acid dissolution followed by atomic absorption analysis. Recently, inductively coupled plasma atomic emission spectrometry (ICP-AES) has made a significant impact in the elemental analysis field and has been applied to a wide variety of environmental samples[1-7]. Noteworthy features of the ICP technique include the applicability to metals and non-metals, a high sensitivity for all elements with a single set of plasma operating conditions, a simultaneous multielement capability, a wide dynamic range and a relative absence of matrix interference. The primary objective in the certification process is the attainment of accuracy and from this point of view the relative freedom from matrix interference is a particularly significant feature of ICP-AES.

Matrix interference effects in ICP emission spectrometry are small compared to those for other instrumental techniques such as a d.c.arc and spark emission spectrometry and atomic absorption spectrometry. In the analysis of sediment samples, however, certain types of interference primarily associated with the major matrix components readily occur and as a result accuracy and precision are degraded. First, it is important to characterize and quantify the effects and for this it is necessary to distinguish between the physical interference effects, i.e., those related to nebulization and sample introduction, and spectral interference effects which originate in the plasma.

In the case of plasma interference effects, the possibility of spectral line interference and instrumental stray light effects are of concern and have been well documented[8,9]. Chemical and ionization interferences, a feature of atomic absorption spectrometry, are unimportant. Spectral line interference which results when non-analyte emission reaches the detector is common to all emission techniques (rare in atomic absorption spectrometry) and flexibility in wavelength selection is a desirable feature in plasma instrumentation. When spectral interference is unavoidable, quantification of the interference and correction (usually computer-assisted) may provide valid data. This lack of specificity for the plasma technique is an undesirable feature and generally for geological samples such as rock materials and sediments the potential for direct spectral line interference is high relative to other matrix types such as biological materials.

In all optical emission techniques the use of analytical lines that are free from spectral interference is preferred. For the determination of major and minor elements such as Al, Fe, Ti, Ca and Mg in sediments, ICP-AES may be considered to be an established technique since appropriate concentration ranges for determining such matrix elements can be attained by diluting the sample solution. As a result the chemical composition of the sample is matched to that of the standard solution thus minimising matrix interferences. On the other hand, trace element determinations in sediments are "interfered" or "affected" by the presence of major matrix elements. For example, the Al content (approximately 10 %) in Pond Sediment is three orders of magnitude higher than the Pb content (approximately 100 μg/g) and spectral and physical interference effects may result. Floyd *et al*10) demonstrated that a 1000 μg/ml solution of Al, which would be equivalent to the Al concentration for a 1 g sample of Pond Sediment digested and diluted to 100 ml, increased the intensity of the spectral background in the vicinity of the Pb 220.35 nm spectral line significantly relative to that for distilled water. Without an accurate background correction scheme, the measurement of the emission intensity at the analytical wavelength would result in analytical bias. It was also reported that both the Al 309.27 nm and the Mg 309.30 nm spectral lines seriously interfered with the V 309.31 nm line and for analytical purposes the V 310.23 nm line was chosen because of the absence of any significant spectral interference from matrix elements such as Al, Fe, Mg and Ti.

If spectral interferences are found to be significant and cannot be avoided through alternative wavelength selection, such effects should be quantified and corrected for to obtain valid data. In most cases corrections for spectral line interferences have been made by subtracting the apparent intensities provided by interferents from the net intensity of the element using "correction factors"11-15). Corrections for background shifts in ICP-AES have been achieved by subtraction of background intensities at wavelength positions close to the analytical line10,15,16). Corrections for such interferences have also been made in calibration schemes for ICP-AES by the use of matrix-matched standard solutions7) and geological CRMs as calibration standards18)

In the present report some emphasis is given to the characterization, quantification and correction of spectral and physical interference effects associated with the ICP analysis of Pond Sediment. A number of multielement calibration schemes were used in conjunction with a direct-reading spectrometer but instrumentation based on a SIT detector and an echelle spectrometer (photomultiplier detector) were also of value in this work.

2. *Instrumentation*

Three independent ICP instruments were utilized, a conventional direct-reader, a programmable monochromator system incorporating a silicon intensified target (SIT) detector and an echelle grating mono/polychromator equipped with a rotating quartz refractor plate for wavelength scanning. A brief description of equipment and operating conditions for the three systems are given in Table I.

Table I

Description of Instrumentation and Operating Conditions

	Jarrell-Ash Atom Comp	Purpose Built (computer-controlled)	Echelle type
Spectrometer	Polychromator Dispersion, 0.53 nm/mm in 1st order	Monochromator Dispersion, 0.4 nm/mm in 1st order	Mono/Polychromator Dispersion, order dependent (0.07 nm/mm in 90th order)
Detection	PMT (multichannel)	SIT (single channel)	PMT
Generator	Plasma Therm	Shimadzu	Plasma Therm
Frequency (MHz)	27	27	27
Load Coil	4 turns	2 turns	4 turns
Normal Operating Conditions			
Forward Power (Kw)	1.1	1.6	1.1
Coolant (1/min)	18	10	18
Carrier (1/min)	1	1	0.5
Auxiliary (1/min)	0	1.6	0
Observation Height (mm)	19	17	16
Nebulizer and Uptake Rate (ml/min)	Cross-fow type -1.3	Concentric type -2.5	Concentric type -1.5

The direct-reader system is a commercially available instrument (Jarrell-Ash Atomcomp, Model 975) and has the capability for the simultaneous determination of 28 elements at sensitivity levels which are typically at the part per billion order. The polychromator, a 0.75 m Paschen-Runge unit, contains prealigned photomultiplier tube (PMT) detectors and respective exit slits situated along the focal curve at appropriate wavelength positions. The emission wavelengths for elements programmed into the system are given later. The optimum values of the principal ICP operating parameters, i.e. Rf power, observation height, sample uptake rate, were presented for each element in the previous report19) and are essentially the same as those used in this study.

Novel research instrumentation incorporating a SIT as the primary radiation detector has recently been developed20). The computer-controlled system employs the slew-scan technique whereby the monochromator is programmed to address, in sequence, only the desired emission wavelength (wavelength regions of no interest are rapidly bypassed) to provide a rapid sequential multielement capability.

The SIT consists of an array of light sensitive elements which develop a change pattern on exposure to uv/vis radiation. The change pattern is addressed by a scanning electron beam and through the optical multichannel analyzer (OMA) control unit the signal can be displayed in real time on an oscilloscope or stored in memory for further processing, e.g. signal accumulation. The OMA unit has two separate memory areas (memory A and memory B) for signal storage so that plasma background corrected spectra (A-B mode) can be readily afforded. Such emission spectra are of particular value for the study, classification and correction of plasma interference effects, and it is in this respect that SIT detection offers certain advantages relative to photomultiplier tube detection.

The ICP-echelle spectrometer utilized in this work has recently been developed as a detector for high performance liquid chromatography21). In addition to the background correction capability, the echelle spectrometer is ideal for investigation of spectral interferences because of the high resolving power of the spectrometer. A typical spectral bandpass of approximately 0.007 nm, when the entrance and exit slit widths are 50 μm, offers a distinct advantage for characterization of emission spectra over conventional spectrometers. For wavelength modulation within a short wavelength region, a rotating quartz refractor plate (5.5x7.5x2.0 mm) is situated along the light path, just behind the entrance slit toward the collimating mirror. Rotation of the plate causes a displacement of the projected beam which results in a lateral shifting of the entire spectrum in the focal plane. Therefore, it is possible not only to obtain short wavelength scans in the vicinity of any wavelength available on the polychromator but also to make background measurements and subtractions as part of the analytical process[15,16].

3. *Sample Dissolution*

The ICP technique invariably requires sample to be in liquid form so that for solid sample types a preliminary destruction of the material is required. For dissolution of sediment samples, a standard alkali fusion or acid decomposition using hydrofluoric acid has been extensively employed. There have been several reports[18,22,23] of multielement analysis of silicate rocks by ICP-AES, involving dissolution by a fusion procedure if major constituents are determined. A fusion procedure requires a large amount of fusing salt(s) such as $LiBO_2$ or $NaCO_3$ for complete dissolution of silicates, commonly in the proportions 10:1 to 7:1, so that the resultant solution contains a high concentration of the salt. The concentrated solution would lead to nebulizer clogging in a short time and as a result would cause serious drift in the ICP measurement. For simultaneous determination of major, minor and trace elements, an appropriate flux to sample ratio and dilution factor should be carefully chosen under the conditions where the sensitivity and stability of the ICP instrument are maintained. Floyd *et al*[10]recently reported that a fusion with NaOH in graphite crucibles (at a flux to sample ratio of 10:1) was found to be suitable for preparation of geological and environmental samples for determination of up to 50 elements at major, minor and trace levels by ICP-AES.

An acid dissolution procedure has more frequently been used for pretreatment of sediment samples before ICP analysis. Since sediment samples usually contain a relatively high concentration of organic matter, complete destruction of organic matter is desirable. Removal of organic matter can also eliminate potential spectral interference due to the emission lines of carbon, e.g. the broadened wing of the C 193.091 nm line on the As 193.696 nm line. For this purpose the addition of perchloric acid as well as nitric and hydrofluoric acids has very often been employed. For the determination of non-volatile elements, as an alternative approach, dry-ashing may be effective to remove organic material. When a total analysis is required, a mixture of nitric/hydrofluoric/perchloric acids has been mostly used for dissolution of sediments. It should be noted, however, that certain chromium-containing minerals (e.g. chromite) are not completely dissolved by nitric/hydrofluoric/perchloric acid mixtures[15,22].

ICP nebulization efficiency is sensitive to the final acid and dissolved solids content so that for the decomposition procedure careful control of the dissolution process is required. The final dilution factor should be chosen after consideration of the element concentrations in the digested solution and the respective ICP detection limits. Frequently it is not possible to achieve simultaneous multielement determinations of trace, minor and major elements with a single dilution step. For sediment samples, however, with extremely high concentrations of Al and Fe, an additional dilution of the digest to bring the signal intensities of the elements within the linear range of the calibration curves is normally required.

In this experiment a mixed acid digestion procedure was adopted for dissolution of Pond Sediment. The sample (1 g) was dissolved with a mixture of mineral acids (nitric, hydrofluoric, perchloric acid) and the digest was made up to 100 ml with 0.1 M perchloric acid. Details of the digestion procedure are descibed in Chapter IV.

4. *Determination of Major and Minor Elements*

It is desirable to perform simultaneous multielement analysis for major, minor and trace elements in the Pond Sediment digest, however, as mentioned above, the levels of major and minor elements in the sample solutions (1 g to 100 ml) were too high for direct measurement so that the sample solutions were diluted a further 100 times with 0.1 M perchloric acid. A two-point calibration procedure was adopted to determine major and minor elements: that is, a low standard, 0.1 M perchloric acid and a high standard, 0.1 M perchloric acid containing Al(10), Fe(10), Ti(1), Mg(1) and Ca(1) at μg/ml level. In ICP analysis it is required to match the acid concentration of standard solutions to that of sample solutions in order to eliminate possible differences in sample transport efficiency and plasma excitation mechanisms for the two solutions. In this case, fortunately, the matching of the acid concentration between the sample and standard solutions could be easily achieved by the dilution procedure.

For the determination of Al and Fe, analytical problems in ICP measurement were not found. However, the variations due to incomplete sample dissolution were sometimes observed for Al determinations in Pond Sediment. Complete decomposition of the sample has to be carried out carefully for the determination of Al.

A standard addition method was also employed for the determination of Mg and Ca. The analytical values for Mg and Ca obtained by the two calibration procedures were in good agreement as shown in Table II, indicating that no chemical interference occurred in the determination of Mg and Ca. This is one of the advantages of ICP analysis where both Mg and Ca are completely dissociated into free atoms/ions due to the high temperature of the plasma excitation source. In contrast, serious chemical interferences were found for the Ca and Mg determinations by atomic absorption spectrometry as described in Chapter IV.

Table II

Analytical Values for Major and Minor Elements in Pond Sediment
(wt. %)

Element	Calibration Procedure 2-point calibration	 standard addition	certified or reference values
Al	10.7	–	10.6 ±0.5
Fe	6.62	–	6.53±0.35
Ti	0.623	–	(0.64)
Mg	0.925	0.925	–
Ca	0.816	0.828	0.81±0.06

Rf Power 1.1 Kw; Observation Height, 19 mm;
Sample Uptake Rate, 1.0 ml/min

5. *Determination of Trace Elements*

Before considering procedures used for trace element determinations, the elemental composition of Pond Sediment is reviewed in order to assist in the understanding of spectral and physical interferences. When 1 g of Pond Sediment is digested and made up to 100 ml, typical concentrations for elements are given in Table III.

It is apparent that the concentrations of the matrix elements, particularly Al and Fe, are more than two orders of magnitude higher than those of the trace elements. It can be expected, therefore, that in the analysis of Pond Sediment trace element determinations would be subject to severe spectral interference. Thus the possibility of spectral interference due to the major and minor elements should be carefully investigated before determining the trace elements. In particular, Al, Fe and Ti have complex emission spectra, whose lines may coincide with or overlap the analytical lines of the trace

Table III

Elemental Concentration in the Sample Solution
(1 g Pond Sediment to 100 ml)

Major and Minor Elements			Trace Elements					
Al	1060	μg/ml	Mn	7.7	μg/ml	Ni	0.40	μg/ml
Fe	653		Zn	3.4		Sc	0.28	
Mg	93		V	2.5		Co	0.27	
Ca	81		Cu	2.1		As	0.12	
K	68		Sr	1.1		Sb	0.02	
Ti	64		Pb	1.1		Cd	0.0082	
Na	57		Cr	0.75				

element. Also the major elements may cause significant background shifts in the uv region compared to alkali and alkaline earth elements, thus the respective emission spectra of the three elements have to be examined carefully.

Finally the relatively high dissolved solid content of the solution (approximately 0.2 %) should be taken into account in deciding whether or not physical interference associated with sample transport is prevalent.

a. Spectral Interference

The analytical lines for each element programmed into the direct-reading ICP spectrometer are listed in Table IV. It should be noted that the analytical wavelength for each element will depend on the type of ICP instrumentation and selection of an alternative wavelength may provide more valid data for certain types of matrices such as geological and steel samples. There have been a number of reports on interelement line interferences in ICP-AES and, if necessary, the selection of an alternative analytical line which is free from any significant spectral line interference is recommended.

Spectral interferences in ICP-AES can be classified into two general categories: line overlap and background shifts. When such interferences are significant and unavoidable at the prealigned wavelength, selection of an analytical line which does not suffer from any significant interference should be first considered. A scanning type ICP spectrometer does offer some advantages with respect to wavelength selection, however, it is laborious and time-consuming to ensure that an analytical line is free from interferences for a particular sample type. For a direct-reading ICP spectrometer the analytical lines of appropriate sensitivity and dynamic range are selected after consideration of a wide variety of samples and it would be very inconvenient and

Table IV

Analytical wavelengths for the direct reader ICP Instrumentation

Element	Wavelength (nm)	Element	Wavelength (nm)	Element	Wavelength (nm)
Sn	189.9 (II)	Cd	228.8*	Si	288.2
As	193.7	Co	228.6 (II)	V	292.4 (II)
Se	196.0	Ni	231.6*(II)	Al	308.2
Mo	202.0 (II)	B	249.8	Be	313.0 (II)
Zn	213.9	Mn	257.6 (II)	Ca	317.9 (II)
P	214.9*	Fe	259.9 (II)	Cu	324.8
Sb	217.6	Cr	267.7 (II)	Ti	334.9 (II)
Pb	220.4 (II)	Mg	279.6 (II)	Sr	421.5 (II)

(II) refers to ionic line; * refers to 2nd order expensive to replace the analytical channel of a particular element, when spectral interference was subsequently "discovered". Corrections for both categories of spectral interference have been made by applying previously determined "correction factors" which are ratios of the sensitivity of a particular line for the interferent to that for the analyte. This is the only convenient way to deal with spectral interferences and can be achieved by subtracting the apparent intensity provided by the interferent(s) from the net intensity of the affected element. Usually, the solution of an individual element prepared from high purity metal or metal-salt is introduced into the plasma, and then the intensity registered at the channel of the element of interest is expressed as the interference factor.

The study of spectral interferences as outlined above involve both spectral line and background interferences and it is not possible to distinguish between them. Recent developments of ICP instrumentation have made it possible to separate the two components by measuring either or both side(s) of the analytical line of the desired element, assuming that background shifts usually exhibit broad spectra, or by scanning the entire spectra of the element and interferents in the region adjacent to the analytical line. Generally speaking, however, it is rather laborious work to characterize and quantify spectral interferences in ICP-AES for combinations of elements and diverse concentrations.

Individual solutions of the matrix elements at concentrations corresponding to that in the Pond Sediment digest were prepared in order to quantify spectral interferences by the matrix elements. Mutual line interference among trace elements was considered to be not significant. A mixed solution which contained all the matrix elements at the same concentrations as the individual solutions was also prepared. The high purity metals (99.99–99.999 % for Al, Fe, Ti and Mg) or the high purity metal-salts (99.99–99.999 % for Na, Ca and K) were dissolved in high purity acids or sub-boiling water, and then the solutions were diluted to the indicated concentrations in Table V with 0.1 M perchloric acid. In determining correction factors, it is essential to ensure that the solutions of the interfering element do not contain significant amounts of the analyte as an impurity. An adequate rinse of the nebulizer chamber is also important to remove memory effects due to the high concentration of the previously aspirated interferent.

The direct-reading ICP spectrometer was standardized by a 2-point calibration procedure, using a low standard (0.1 M perchloric acid) and a high standard (0.1 M perchloric acid containing 10 or 1 μg/ml of the trace elements listed in Table V), and then each of the individual and mixed solutions of the matrix elements was aspirated into the plasma at intervals of not less than 5 min, with a distilled water rinse between each solution. The apparent intensities for each of the trace elements provided by each and all of the matrix elements were printed out in concentration units. It was necessary to operate the instrument under exactly the same conditions as used in subsequent analyses, because the correction factors may be quite sensitive to changes in certain of the principal ICP operating parameters, notably the power and the carrier gas flow rate15). The correction factors were also checked at appropriate intervals.

Table V summarizes the results for the spectral interferences caused by the major and minor elements on each of the trace elements. The numerical values in the table are expressed in μg/ml units, for example, a 900 μg/ml single solution of Al provides an apparent concentration of 0.58 μg/ml on the Mo channel (202.0 nm).

As shown in Table V, Ca and Mg cause almost no spectral interferences at the wavelengths examined. The stray light effects, which result in positive background shifts due to the intense ion lines of the alkaline earth elements, can be considered in this case to be not significant. The concentration of Ti in the Pond Sediment solution is relatively low, however, a Ti solution of 60 μg/ml did provide a severe interference corresponding to 0.12 μg/ml of Co. The interference by Ti on the Co analytical line has been studied using two other independent ICP spectrometers and are presented and discussed as a case study in the next section. Iron and Al are the main interfering elements due to their rich emission lines and high concentrations. Iron causes severe interference on the Sn, As, Se, Pb, B and V channels, while Al gives interference on the analytical lines of Sn, As, Se, Mo and Pb. Besides line overlap, background shifts caused by the matrix elements are included in the factors given in Table V.

Table VI presents the possible spectral line interferences by matrix elements on each of the trace elements. If the matrix effects are due to only spectral interference, the sum of the five factors, which are provided by each of the five interferents, for each of the trace elements would be the same as the factor given for the element by the mixed solution (sum/mix=1). As can be seen in Table V, however, the factors obtained with the mixed solution result in lower values for all the elements (except for Mn) than the corresponding sums of the five factors. Particularly, some elements, i.e. Zn, Cd, Co, Ni and B, show significantly greater sum/mix ratios than 1.0. These results indicate that physical interferences due to changes in sample transport efficiency and/or plasma excitation mechanisms as a result of the higher dissolved solids content of the mixed solution were significant. Such physical interference problems are discussed later in this chapter.

The results for trace elements in Pond Sedimet using correction factors are first considered. For this purpose the interelement correction factor and the

Table V Spectral Interferences by Matrix Elements

		Spectral Interference BY							
ON	(nm)	Mg(80)	Ca(60)	Ti(60)	Fe(600)	Al(900)	Sum[1]	Mix[2]	Sum/Mix
Sn	189.9(II)	0.0875	–[3]	0.4620	0.4318	2.433	3.414	3.237	1.05
As	193.7	0.0067	–	–	0.3331	15.75	16.09	15.49	1.04
Se	196.0	0.0062	–	–	0.8147	3.806	4.627	4.459	1.04
Mo	202.0(II)	0.0073	–	–	0.0606	0.5804	0.6483	0.6213	1.04
Zn	213.9	0.0325	–	0.0040	0.0887	0.0410	0.1662	0.1547	1.07
Pb	220.4(II)	0.0473	0.0034	0.0532	0.5264	1.611	2.241	2.128	1.05
Cd	228.8	0.0024	–	0.0005	0.0163	0.0099	0.0291	0.0267	1.09
Co	228.6(II)	0.0095	0.0023	0.1212	0.0807	0.0160	0.2297	0.2033	1.13
Ni	231.6(II)	0.0263	0.0011	0.0003	0.0763	0.0074	0.1114	0.0926	1.20
B	249.8	0.0428	0.0446	0.0621	1.063	0.0518	1.264	1.029	1.22
Mn	257.6(II)	0.0059	–	–	0.0253	0.0363	0.0674	0.0703	0.96
Cr	267.7(II)	0.0078	0.0014	0.0114	0.0496	0.0201	0.0903	0.0883	1.02
V	292.4(II)	0.0119	0.0013	0.0405	0.1199	0.0010	0.1746	0.1694	1.03
Be	313.0(II)	0.0001	0.0001	0.0080	0.0008	0.0003	0.0093	0.0092	1.01
Cu	324.8	0.0092	0.0059	0.0617	0.0106	0.0103	0.0977	0.0953	1.02
Sr	421.5(II)	–	0.0073	–	0.0010	–	0.0083	0.0081	1.02

1. Sum of the values given by the five interferents
2. Mixed solution containing Mg(80), Ca(60), Ti(60), Fe(600) and Al(900) at μg/ml level.
3. Not detected.

All values are expressed in μg/ml units. To calculate usual correction factors, divide the value for each of trace elements by the concentration of each of the interferents.

Table VI

Possible Spectral Line Interferences by Major Elements

On	(nm)	By	
Mo	202.030 (II)	Fe	202.052
Zn	213.856	Fe	213.859; Ti (unknown line); (Cu 213.851)
Pb	220.351 (II)	Al	220.463 (line wing); Fe 220.346; Ti (unknown line)
Co	228.616 (II)	Ti	228.618; Fe 228.615
Cd	228.802	Fe	228.763, 228.725
Mn	257.610 (II)	Al	257.510; Fe 257.574, 257.669, 257.687
Cr	267.716 (II)	Fe	267.688; P 267.712; (Mn 267.725)
V	292.403 (II)	Fe	292.385; Ti (unknown line)
Cu	324.754	Fe	324.721, 324.728, 324.739; Ti 324.860 (line wing); (Mn 324.754)

concentration of the affecting element must be measured correctly. The correction factors given in Table V were almost the same as those obtained in earlier studies using 1000 μg/ml pure solutions of a single element and, therefore, suggests that the interference effects exhibit some degree of linearity.

The direct-reading ICP spectrometer was standardized by a 2-point calibration procedure (see page 55) and then the sample solutions of Pond Sediment (1 g to 10 l for matrix elements, 1 g to 100 ml for trace elements) were introduced to the plasma for multielement analysis of major, minor and trace elements. The trace element data as determined above include both real and apparent intensities so that the corrected values were obtained by subtracting the corresponding total apparent concentrations (calculated using the factors in Table V and the concentrations of the matrix elements previously determined) from the net concentrations for each element.

Table VII presents the raw (not-corrected) and the corrected values for trace elements in Pond Sediment. The analytical values for the elements obtained using correction factors are in fairly good agreement with the certified or reference values. However, since the approach does not take into account differences in sample transport efficiency between samples and standards, there is the tendency to obtain slightly low values for most of the trace elements. Additional dilution of the sample solutions (1 g to 100 ml) may eliminate this effect.

In the case of Cr, a significantly lower value than the certified value was obtained after correction. It is well-known that certain Cr-containing minerals such as chromite are not completely dissolved by the acid dissolution system used in this experiment[15,22]). It has also been demonstrated that in the presence of perchloric or hydrochloric acid Cr may readily vaporize as CrO_2Cl_2 during heating[24]). The low value of Cr determined by ICP-AES may be explained by incomplete dissolution or analyte loss, though it is not clear at this stage which of the two is predominate.

Table VII

Correction of Spectral Interferences by Correction Factor Method

Element	Raw Data	Corrected Data	Certified or Reference Values
Mn (μg/g)	828	790	(770)
Zn	348	326	343±16
Cu	208	201	210±12
V	259	228	(250)
Sr	105	103	(110)
Pb	210	97	105±6
Cr	75.0	61.1	75±5
Ni	43.0	34.5	40±3
Co	50.8	26.0	27±3

b. Case Study: Spectral Interference by Ti on Co

As previously shown in Table V, Ti generates significant spectral interference on the Co 228.6156 nm analytical line, for example, a 60 μg/ml solution of Ti provides an apparent intensity corresponding to 0.12 μg/ml of Co. The interference by Fe on the Co line is also demonstrated but to less an extent. The analytical value for Co obtained by the 2-point calibration procedure was 51μg/g, while the certified value for Co in Pond Sediment is 27±3 μg/g. Although a consistent value for Co was obtained through the correction using correction factors, further investigations were undertaken to clarify the interference. For this purpose two independent ICP spectrometers, a programmable monochromator system incorporating a SIT detector and an echell mono/polychromator which has a capability of wavelength scanning by rotation of a quartz refractor plate, are utilized. A description of the instruments and operating conditions are given in section 2 (see page 49).

In Fig 1, ICP emission spectra for Pond Sediment digests obtained by SIT detection are presented. The upper spectrum was recorded for a digest of Pond Sediment (1g to 100 ml) and emission lines of a number of elements, particularly Al, Fe and Ti, are contained within the spectral region 228 nm to 232 nm. The upper spectrum (A) was stored in memory A of the OMA control unit for further processing. Next the spectrum for a composite solution containing Al, Fe, Ti, Ca and Mg which was recorded at the same concentrations as those in the sample solution was stored in memory B. The subtracted spectrum (memory A-memory B) removes the emission lines of the matrix elements and thus the interference-free Co emission line (228.616 nm) is presented on the lower spectrum (B). The peak height of the Co line corresponds to 27 μg/g of Co, coincident with the certified value. A further interesting feature to note is that the baseline of the upper spectrum does not coincide with the zero intensity level. This rise in the plasma background level, due to wings of many emission lines, continuous emission background and/or stray lights, is fortunately cancelled out in the lower spectrum by the above-mentioned procedure. It has been pointed out that the signal to noise ratio for SIT detection in ICP-AES at wavelengths less than 250 nm is much poorer than for photomultiplier detection[25)].

The high wavelength resolution capability of the echelle spectrometer was next applied to spectral analysis. Wavelength scanning in the vicinity of the Co analytical line was performed by rotation of the quartz refractor plate placed just behind the entrance slit. The spectrometer is essentially the same as that used by McLaren and Berman[16)]. Individual solutions of Al (1000 μg/ml), Fe (1000 μg/ml), Ti (1000 μg/ml), Co (1 μg/ml) and the digest of Pond Sediment (0.9 g to 100 ml) were sprayed into the plasma, and the respective emission spectra were recorded within the wavelength region 228.616±0.010 nm. Fig 2

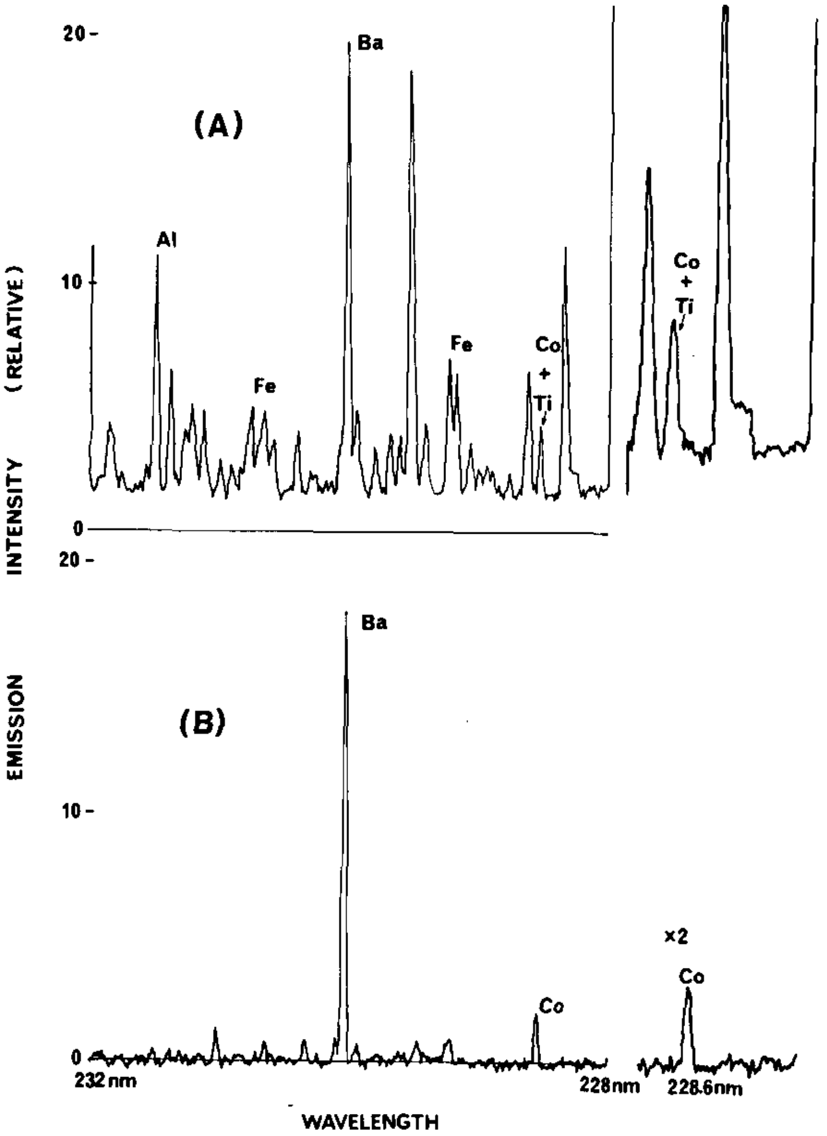


Fig 1. SIT emission (ICP) spectra for Pond Sediment, correction for spectral interference by Ti (228.618 nm) on Co (228.616 nm).

(A) A mode: Pond Sediment digest

(B) A–B mode: Background corrected

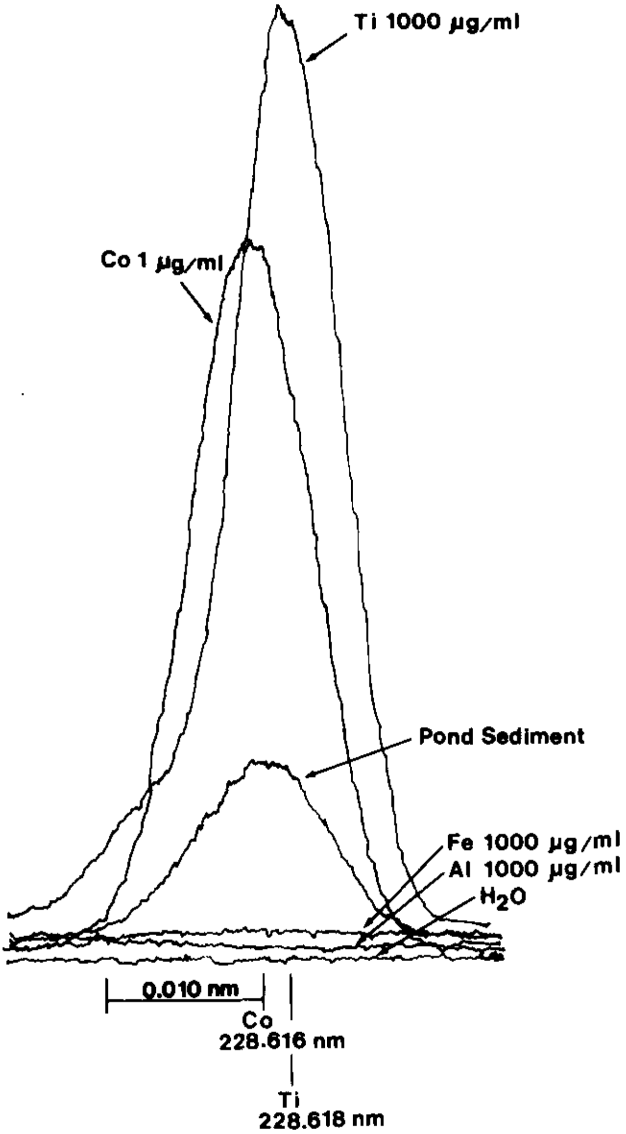


Fig 2. Wavelength scans (with an ICP-echelle monochromator) in the vicinity of the Co 228.616 nm line demonstrating exact overlap by the Ti 228.618 line.

shows the ICP emission spectra adjacent to the Co 228.616 nm analytical line for each of the solutions. Fe and Al cause slight background enhancements due to continuous broad-band emission. The emission line of Ti at 228.618 concides exactly with the Co line at 228.616 and thus it is not possible to eliminate the Ti interference. As shown in Fig 2, the emission spectrum of Pond Sediment digest exhibits a rather expanded peak reflecting the overlap between both lines. For the determination of Co in the Pond Sediment digest an appropriate correction factor for Ti was subtracted from the peak intensity at 228.616 and a consistent value for Co (24 μg/g) was obtained.

In order to specify and quantify plasma interferences, the use of the abovementioned instruments and procedures is desirable but very often such approaches lack a simultaneous multielement analysis capability. The limited availability of such instruments also detracts from their use on a more widespread basis. Appropriate selection of an alternative analytical line which is free from significant interference is the main approach to avoid spectral interference but a loss in sensitivity may have to be accepted. As an alternative Co line, for example, the 238.892 nm line has often been used, however, the latter suffers from large interelement interference by the Fe 238.863 nm emission line12). Recently, Uehiro26) found that the Co 230.786 line was free from spectral line interferences except for Ni 230.779 nm line. The concentrations of Co and Ni are usually comparable for most geological samples, and therefore, the contribution of the Ni line interference to the Co line can be considered small (correction factor, Ni/Co=1×10^{-3}).

c. *Physical Interferences*

Physical interferences in ICP-AES generally involve changes in sample transport efficiency and plasma excitation mechanisms, usually due to differences between the dissolved solids contents of samples and standard solutions. Sample uptake rate may be controlled exactly by the use of a peristaltic pump or by careful control of the carrier gas flow rate, but the efficiency of mist transport after sample nebulization may change mainly depending on the viscocity or dissolved solids content of sample solutions. Differences in dissolved solids contents between sample and standard solutions may lead to analytical bias. Therefore, special attention should be paid to such physical interferences when trace elements are determined in the presence of much higher concentrations of major and minor elements.

One approach to correct for physical interferences is to adopt an internal standard method. Reference elements used for this purpose have so far been little studied, primarily because the ICP discharge is very stable and emission signals have good stability. It is considered, however, that matrix effects and effects due to instrumental instability, including those related to the sample introduction system, could be reduced by the use of suitable reference elements. Odegard[13)] recently reported that Li and Y were suitable as reference elements not only because they fulfilled low and high excitation requirements respectively but also because these elements were rare and seldom analyzed in sediment samples.

In this study, physical interferences related to sample transport efficiency were investigated by changing the dilution factors of the sample solutions. The original solutions (1 g to 100 ml, x100) were additionally diluted 2.5, 5 and 10 times with 0.1 M perchloric acid and a 2-point calibration procedure was employed, using a low standard (0.1 M perchloric acid) and a high standard (0.1 M perchloric acid containing 10 or 1 μg/ml of the trace elements listed in Table VIII), to determine trace elements in the four (x100, x250, x500, x1000) solutions. The concentration levels of certain trace elements in the prepared solutions, however, became near the respective detection limits of the ICP spectrometer.

Table VIII demonstrates the effects of sample dilution factors on the determination of trace elements in Pond Sediment, where the results are expressed as the ratios to the concentrations in the x100 solution. The results for all the trace elements increase with sample dilution, suggesting that physical interferences related to sample transport efficiency are significant for the x100 solution. Appropriate dilution of sample solution may provide more valid data for trace element determinations if the reliability and sensitivity of the calibration curves are maintained. The relative intensities for x250 to x1000 solutions are almost constant, being approximately 10 % higher than that for x100 dilution. Although much work on geological samples has been made for x100 solutions, x250 dilution (1 g to 250 ml) may be more suitable for trace element determination in Pond Sediment. Tao *et al*[27)] recommended x250 dilution for the analysis of Pond Sediment by ICP-AES.

Table VIII Effect of Dilution on the Determination of Trace Elements in Pond Sediment

Element	Dilution Factor			
	x100*	x250	x500	x1000
Zn	1	1.06	1.09	1.11
Pb	1	1.07	1.12	1.13
Co	1	1.10	1.16	1.18
Ni	1	1.08	1.15	1.20
Mn	1	1.07	1.10	1.13
Cr	1	1.06	1.09	1.13
V	1	1.07	1.10	1.10
Cu	1	1.07	1.09	1.09
Sr	1	1.08	1.10	1.10
Sc	1	1.06	1.09	1.11

* 1 g to 100 ml solution; the values are expressed as the ratios to the x100 solution. Spectral interferences were previously corrected, using the correction factors given in Table V, before calculation. A digest of Pond Sediment (1 g to 100 ml, x100) was diluted additional 2.5 (x250), 5 (x500) and 10 (x1000) times with 0.1 M perchloric acid.

Spectral interferences may be corrected by the procedures mentioned earlier, however, it is more difficult to characterize and quantify physical interferences in ICP-AES. One way to reduce these problems is to do an appropriate dilution of sample solutions as much as possible in order to match the nature of both sample and standard solutions. Another approach is to add reference elements to sample solutions as internal standards to compensate for such physical interferences. Further investigations are required to clarify physical interferences in ICP-AES.

d. Use of Matrix-matched Standards for Calibration

As already mentioned, complex interference effects may be operating during ICP measurement so that in practice it is very difficult to charaterize and quantify the various components. One way to correct for matrix effects is to use "matrix-matched" standard solutions for calibration, that is solutions which contain matrix elements at the same concentrations as those in the sample solutions. By adopting this method, the nature of both sample and standard solutions can be matched and as a result physical interferences related to nebulization and sample transport are cancelled. Spectral interferences by matrix elements are also compensated for because the apparent intensities for trace elements provided by matrix elements can be accomodated in the calibration scheme. Uchida *et al*17) successfully determined several trace elements in silicate rocks by the use of matrix-matched standards.

Although the matrix-matched procedure can be expected to provide valid analytical data, the concentrations of major and minor elements in the sample solutions must be known before preparing the standard solutions. Fortunately, the multielement analysis capability of the ICP technique can readily provide information on matrix element concentrations. For routine analysis, however, this procedure would be applicable only when the matrices of samples to be analyzed are of similar composition.

In this experiment the determination of trace elements in Pond Sediment was carried out employing a 2-point calibration procedure, where matrix-matched solutions were used for low and high standards. Table IX shows the elemental composition of the low and high standards. High purity metals or metal-salts were used for the preparation of the standard solutions to reduce the possibility of analyte contamination. Even in the presence of the high concentrations of matrix elements, instrumental drift and fluctuation of emission signals were insignificant over the one hour analysis period.

The analytical values obtained through the use of the matrix-matched standard solutions are given in Table X. The values are in good agreement with the certified or reference values for Pond Sediment, indicating that this calibration procedure is quite useful for overall correction of the various types of matrix interference in ICP-AES. Because a certified reference material is a homogeneous material by definition, a matrix-matched procedure is always valid and of use in the CRM field. ICP-AES coupled to this calibration scheme may provide highly accurate results for the CRM certification process.

Table IX
Composition of Matrix-matched Standard Solutions

Element	Low Standard	High Standard	Element	Low Standard	High Standard
Al	1000	1000	P	–	20
Fe	600	600	Mn	–	10
Mg	80	80	Zn	–	4
Ca	80	80	Cu	–	2
Ti	60	60	V	–	2
K	60	60	Pb	–	2
Na	60	60	Cr	–	1
			Co	–	1
			Ni	–	1
			Sr	–	1

Units, μg/ml; Low and High Standards, 0.1 M perchloric acid

e. Use of Solvent Extraction

The solvent extraction system, sodium diethyldithiocarbamate (DDTC) and methylisobutylketone (MIBK), was employed to extract and concentrate certain heavy metals and, at the same time, to remove matrix elements. Details of this procedure have been described in the previous chapter but it should be noted that simultaneous extraction by a solvent extraction technique is usually restricted to only a few elements, depending on solvent, chelating reagent and extraction conditions. The direct nebulization of MIBK solution into the plasma has not been successfully performed with the direct-reading ICP spectrometer, so that the acid digested solutions, after evaporation of MIBK, were used to determine trace elements. It was noted that the concentrations of major elements in the final extracts were at insignificant levels with respect to spectral interference.

The analytical values obtained by the DDTC-MIBK extraction system are presented in Table X and it can be seen that there is good consistency with the certified or reference values. Cadmium in Pond Sediment could not be determined by the correction factor and matrix-matched methods due to inadequate ICP sensitivity and the occurrence of matrix effects. For example, the Cd 228.802 nm line is subject to spectral interference by the As 228.812 nm line[16]), and in typical sediments the relative concentration of As is much higher than Cd. Only the solvent extraction approach provided an accurate value for Cd. Solvent extraction was also applicable to Zn, Cu, Pb, Ni and Co.

Table X
Comparison of Analytical Results for Trace Elements Obtained by Correction Factor,
Matrix-matched and Solvent Extraction Procedures

Element	Correction Factor	Matrix matched	Solvent extraction	Certified or reference values
Mn (μg/g)	790	798	–	(770)
Zn	326	348	338	343±16
Cu	201	220	221	210±12
V	228	254	–	(250)
Sr	103	107	–	(110)
Pb	97	110	108	105± 6
Cr	61.1	67.7	–	75± 5
Ni	34.5	41.8	41.7	40± 3
Co	26.0	27.8	26.4	27± 3
Cd	–	–	0.81	0.82± 0.06

6. *Conclusion*

ICP-AES has been used for elemental analysis of Pond Sediment. An acid dissolution procedure with a mixture of nitric, hydrofluoric and perchloric acids has been employed for the dissolution of Pond Sediment. The analytical values obtained by dissolution and ICP analysis are generally in good agreement with the certified or reference values after appropriate corrections. A relatively low value was obtained for Cr due to probably to incomplete dissolution of the sample or loss of the element during heating.

An investigation on sample dilution revealed that a dissolved solids content corresponding to 1 g of Pond Sediment in 250 ml is most appropriate to reduce physical interference.

Corrections for spectral interferences using correction factors, matrix-matched standards or solvent extraction were investigated. The correction factor method is convenient for a *direct-reading ICP spectrometer* and provides fairly good analytical data. For this purpose correction factors and concentrations of interfering elements must be measured correctly and an appropriate sample dilution factor should be selected to reduce physical interferences. The matrix-matched method, where overall matrix effects are cancelled out in the calibration scheme, is quite useful for samples of the same chemical composition but the possibility of introducing analyte contamination during solution preparation must be considered. Solvent extraction is of value when ICP sensitivity becomes the limiting factor. Also the approach may be applicable to only a few elements.

Detailed investigations of spectral interference in the case of Co were performed with an SIT-OMA detection system and an echelle spectrometer equipped with a quartz refractor plate. Both instruments were useful for characterization and quantification of spectral interference due to line overlap and background shifts.

References

1) Moselhy,M.M., Boomer,D.W., Bishop,J.N., Diosady,P.L. & Howlett,A.D. (1978): *Can. J. Spectrosc.*, 23, 186
2) Berman,S.S., McLaren,J.W. & Willie,S.N. (1980): *Anal. Chem.*, 52, 488
3) Manzoori,J.L. (1980): *Talanta*, 27, 682
4) Lechler,P.J., Roy,W.R. & Leininger,R.K. (1980): *Soil Sci.*, 130,238
5) Sturgeon,R.E., Berman,S.S., Desaulniers,J.A.H., Mytytiuk,A.P., McLaren,J.W. & Russel,D.S. (1980): *Anal. Chem.*, 52,1585
6) McLeod,C.W., Otsuki,A., Okamoto,K., Haraguchi,H. & Fuwa,K. (1981): *Analyst*, 106, 419
7) Moselhy, M.M., & Vijan,P.N. (1981): *Anal. Chim. Acta,* 130, 157
8) Fassel,V.A. (1978): *Science*, 202, 183
9) Dahlquist,R.L. & Knoll,J.W. (1978): *Appl. Spectrosc.*, 32, 1
10) Floyd,M.A., Fassel,V.A. & D'Silva,A.P. (1980): *Anal. Chem.*, 52, 2168
11) Boumans,P.W.J.M. (1976): *Spectrochim, Acta*, 31B, 147
12) Marciello,L. & Ward,A.F. (1978): *Jorrell-Ash Plasma Newsletter*, 1, (2), 12
13) ϕ degard,M. (1981): *J. Geochem. Exploration*, 14, 119
14) Crock,J.G. & Lichte,F.E. (1982): *Anal. Chem.*, 54, 1329
15) McLaren,J.W., Berman,S.S., Boyko,V.J. & Russel,D.S. (1981): *Anal. Chem.*, 53, 1802
16) McLaren,J.W.&Berman,S.S. (1981): *Appl. Spectrosc.*, 35, 403
17) Uchida,H., Uchida,T & Iida,C. (1980): *Anal. Chim. Acta*, 116, 433
18) Walsh,J.N. (1980): *Spectrochim. Acta*, 35B, 107
19) McLeod,C.W., Furuta,N. & Nishikawa,M. (1980): *Research Report from NIES*, No.18, p33
20) Furuta,N., McLeod,C.W., Haraguchi,H. & Fuwa,K. (1979): *Bull. Chem. Soc. Jpn.*, 52, 2913
21) Uehiro,T. (1981): *Abst. 9th. Inter. Conf. Atomic Spectrosc.*, p44
22) Burman,J-O., Ponter,C. & Bostrom,K. (1979): *Anal Chem.*, 50, 679
23) Burman,J-O. & Bostrom,K. (1979): *Anal. Chem.*, 51, 516
24) Agemian,H. & Chau,A.S.Y. (1976): *Analyst*, 101, 761
25) Furuta,N., McLeod,C.W., Haraguchi,H. & Fuwa,K. (1980): *Appl. Spectrosc.,* 34, 211
26) Uehiro,T.: Personal communication
27) Tao,H., Iwata,Y., Nojiri,Y., Hasegawa,T., Haraguchi,H. & Fuwa,K.: *Bull. Chem. Soc. Jpn.*, submitted

CHAPTER VI

Analysis of Pond Sediment and Rock Reference Materials by Instrumental Neutron Activation Analysis with the Use of Neutron Spectrum Monitors

T. Takamatsu, M. Kawashima, R. Matsushita and M. Koyama.

1. *Introduction*

Neutron activation analysis (NAA) has been applied successfully to a wide variety of complex environmental samples for trace element analysis. Because of its excellent sensitivity for many elements and general lack of matrix effects, instrumental neutron activation analysis (INAA) has been used to determine up to 30 elements in diverse environmental samples such as biological materials, soils and sediments.

Instrumental neutron activation analysis can be classified into two categories with respect to the sort of standards used and consequently to the method of calculation of elemental content. One approach is the so-called "relative method" in which samples are irradiated together with standards containing the elements to be determined. The calculation is straightforward in that it just involves comparing the total absorption peak areas normalized to the cooling periods for both samples and standards. The other approach is sometimes called the "absolute method", the "flux monitor method", or the "comparator method". Depending on the number of comparators used, terms such as single comparator or multicomparator method are used. In principle, the method for determination is based on a calculation using nuclear data such as cross sections and γ-ray abundances and also experimental data such as efficiencies for counting γ-rays and neutron fluxes which are determined by the use of flux monitors of a limited number.

Both methods have merits and limitations. In the relative method, it is inconvenient to prepare the appropriate combination of standards which cover all the elements to be determined in a given sample. However, the determination can be carried out without any knowledge of nuclear data, neutron flux, neutron spectra and detector efficiencies.

The latter method initially developed by Meinke et al. 1) makes use of only one flux monitor to determine all the elements in a sample. This method is, however, theoretically valid only when the neutron spectra, that is the thermal and the epithermal neutron fluxes, are known. Uncertainty associated with nuclear data and the efficiency of a detector will also lead to inaccurate results. However, consistency of the results are maintained as long as the same experimental conditions and nuclear data are used.

Girardi *et al.*[2)] studied the "absolute" method by using cadmium ratios and cobalt as a monitor. Kim *et al.*[3)] measured cadmium ratios to determine the thermal and epithermal neutron fluxes before or during irradiation of samples. Hoste *et al.*[4)] have proposed a combination of flux monitors consisting of elements which are sensitive to thermal and/or epithermal neutrons such as cobalt and gold, and ruthenium isotopes ^{96}Ru, ^{102}Ru and ^{104}Ru. Schmidt *et al.*[5)] added iron to ruthenium. The methods of the latter two are theoretically excellent from the view point that neutron spectra and fluxes can be determined for every irradiation without any special device for irradiation, such as cadmium covered irradiation in addition to non-covered ones.

The present method applied to the analysis of Pond Sediment and rock reference materials is based on the estimation of not only neutron fluxes but also neutron temperatures by using a set of monitors consisting of cobalt, lutetium, antimony and uranium.

2. *Theoretical*

According to the Westcott formalism[6)], the effective cross section of a given nuclide can be expressed as follows by assuming that the distribution of the thermal neutron energy is Maxwellian and that of the epithermal is 1/E.

$$\hat{\sigma} = \sigma_0 g + \sqrt{\frac{4T}{\pi T_0}}\, rI' \qquad (1)$$

or

$$= \sigma_0(g + rs) \qquad (2)$$

$$s = \frac{1}{\sigma_0}\sqrt{\frac{4T}{\pi T_0}}\, I' \qquad (3)$$

where

$\hat{\sigma}$: effective cross section.

σ_0: conventional cross section for neutrons with a velocity of 2200 m/sec.

I' : resonance integral with a certain cut-off energy in which the 1/v tail is subtracted.

r : neutron spectrum index; in well moderated systems, r is reduced to the ratio of epithermal to thermal neutron fluxes.

T_0: 293.59 °K at which the most probable velocity of Maxwellian neutrons become 2200 m/sec.

T : neutron temperature at which the samples are irradiated.

If we introduce a new spectrum parameter r' as follows, r' includes information on the flux ratio and the neutron temperature and s' becomes I'/σ_0 which can be calculated from nuclear data. It is clear, therefore, that s' equals zero and g is unity when the cross section of a nuclide obeys the 1/v law.

$$r' = \frac{\phi epi}{\phi th} \sqrt{\frac{4T}{\pi T_0}} \tag{4}$$

$$s' = \frac{I'}{\sigma_0} \tag{5}$$

3. Method of Calculation of the Spectrum Index from Multi-flux Monitors.

If we calculate the weight of an element by measuring the induced radioactivity when using the conventional thermal cross section and a thermal neutron flux, the following expressions hold:

$$W'_1 = A_1 M_1 / C_1 nv_o \sigma_1 \tag{6}$$

$$W'_2 = A_2 M_2 / C_2 nv_o \sigma_2 \tag{7}$$

where

W'_i: weight of an element calculated by using the conventional cross section (σ_i)

A : measured radioactivity.

M : atomic weight of an element.

C : factor for normalizing radioactivity production and decay, detector efficiency, γ-ray branching ratio, isotopic abundance, Avogadro number, etc.

nv_o: thermal neutron flux: an arbitrary number can be used, in case samples and monitors are irradiated together and only the spectrum index is needed.

σ_i : conventional cross section for neutrons of the velocity of 2200 m/sec.

The true weight must be expressed by using the effective cross section in a similar manner to the above.

$$W_1 = A_1M_1/C_1nv_o\sigma_1 \tag{8}$$

$$W_2 = A_2M_2/C_2nv_o\sigma_2 \tag{9}$$

$$\hat{\sigma}_i = \sigma_i(g_i + r's'_i) \tag{10}$$

The ratio W'_i/W_i becomes the ratio of the conventional thermal cross section to the effective thermal cross section. By taking the ratio for two nuclides, a new quotient F can be obtained:

$$F = \frac{W'_1/W_1}{W'_2/W_2} = \frac{g_1 + r's'_1}{g_2 + r's'_2} \tag{11}$$

If we choose a pair of nuclides which have g factors close to unity and s' values quite different, the spectrum index r' can be easily obtained:

$$r' = \frac{F - 1}{s'_1 - Fs'_2} \tag{12}$$

In the case where a reference neutron field such as a thermal column is available, uncertainty regarding the detector efficiencies and nuclear data can be cancelled out as long as the same measuring conditions are used. Let us assume that the g factors of monitors are close to unity and the neutron field is purely thermal. F_{th}, experimentally obtained, can be expressed as in the equation below in which each C'_i obtained by correcting growth and decay of radioactivity is not required to be known.

The correction factor for uncertainty on nuclear data can be obtained by Eq. (13) and the quotient F' instead of F by Eq. (14).

$$Fth = \frac{W'_1/W_1}{W'_2/W_2} = \frac{C'_1}{C'_2} \tag{13}$$

$$F' = F/Fth \tag{14}$$

Once r' is obtained, the neutron temperature can be evaluated by measuring the ^{177}Lu monitor.

$$W'_{Lu}/W_{Lu} = g_{Lu} + r's'_{Lu} \tag{15}$$

In Table I g values of several nuclides are shown as a function of temperature together with effective cross sections.

Table I

g Factors and Effective Cross Sections for Several Nuclides

Nuclide	^{59}Co	In		^{197}Au		^{176}Lu		^{238}U	
Temp. °C	$\hat{\sigma}$	g	$\hat{\sigma}$	g	$\hat{\sigma}$	g	$\hat{\sigma}$	g	$\hat{\sigma}$
20	39.24	1.019	316.0	1.005	150.6	1.701	3631	1.002	4.490
40	39.31	1.023	320.6	1.006	152.4	1.837	3885	1.002	4.608
60	39.37	1.027	325.1	1.008	154.2	1.977	4146	1.002	4.708
80	39.43	1.031	329.1	1.009	155.9	2.118	4409	1.003	4.722
100	39.49	1.035	333.9	1.010	157.6	2.258	4673	1.003	4.833
200	39.77	1.056	355.0	1.015	165.4	2.907	5915	1.005	5.389
300	40.02	1.078	375.2	1.021	172.5	3.418	6912	1.007	5.488
450	40.35	1.113	405.7	1.030	182.1	3.900	7868	1.010	6.490

Effective cross sections are calculated at $r=0.03$ (Westcott's notation)
Unit : barn

Experimental

a. Flux monitors

Appropriate amounts of standard solutions were pipetted out with a micropipette onto either Millipore filters (HAWP 47 mm i.d.) or sheets of aluminum foil of 99.9 % purity. For the analysis of geological reference materials, 50 μg of cobalt, 50 μg of chromium, 20 μg of antimony and 11.3 μg of uranium were spotted onto them. After the droplets of spotted solutions were air-dried, the Millipore filters were sealed in polyethylene bags and packed in sample containers made of polyethylene. Aluminum foils were used for heavy irradiations in a hydraulic facility and Millipore filters were used for pneumatic tube and other irradiations.

b. Samples

Two hundred milligrams of the geological reference materials on average were weighed in sample containers made of clean polyethylene and subjected to irradiation for one hour. Twenty to thirty milligram of those samples were also irradiated in a similar manner for five minutes. Before packing weighed samples into an irradiation capsule, those containers were wrapped with clean polyethylene bags in order to reduce chances of contamination during handling and irradiation. Five of those samples were packed in an irradiation capsule together with the mixed monitors.

c. Irradiation

The geological reference materials were irradiated in the pneumatic facility No.2 of Kyoto University and other samples used for checking the validity of the present method in several facilities are described in Table II.

Table II

Nominal Neutron Fluxes in Irradiation Facilities Used in the Present Work

Irradiation Facility	Neutron Flux (n/cm^2 . sec)			Neutron Temp (°C)
	ϕth	ϕepi	ϕfast	
Hydraulic Tube	8.15×10^{13}	5.95×10^{12}	3.9×10^{13}	100
Pneumatic Tube 1	1.93×10^{13}	6.45×10^{11}	3.2×10^{12}	80
” ” 2	2.75×10^{13}	1.09×10^{12}	6.0×10^{12}	80
” ” 3	2.75×10^{13}	8.40×10^{11}	4.8×10^{12}	80
E-2 Hole	9.00×10^{10}	6.50×10^{7}	1.30×10^{8}	60

d. Measurement

The Ge (Li) detector having an active volume of 40 ml or 60 ml coupled to a NAIG 4K multichannel analyzer was used to measure γ-ray spectra. Efficiency curves were obtained using the IAEA 1 μCi and 10 μCi standard sources.

^{82}Br, ^{24}Na, ^{75}Se and ^{152}Eu were used as well to interpolate and extend data points.

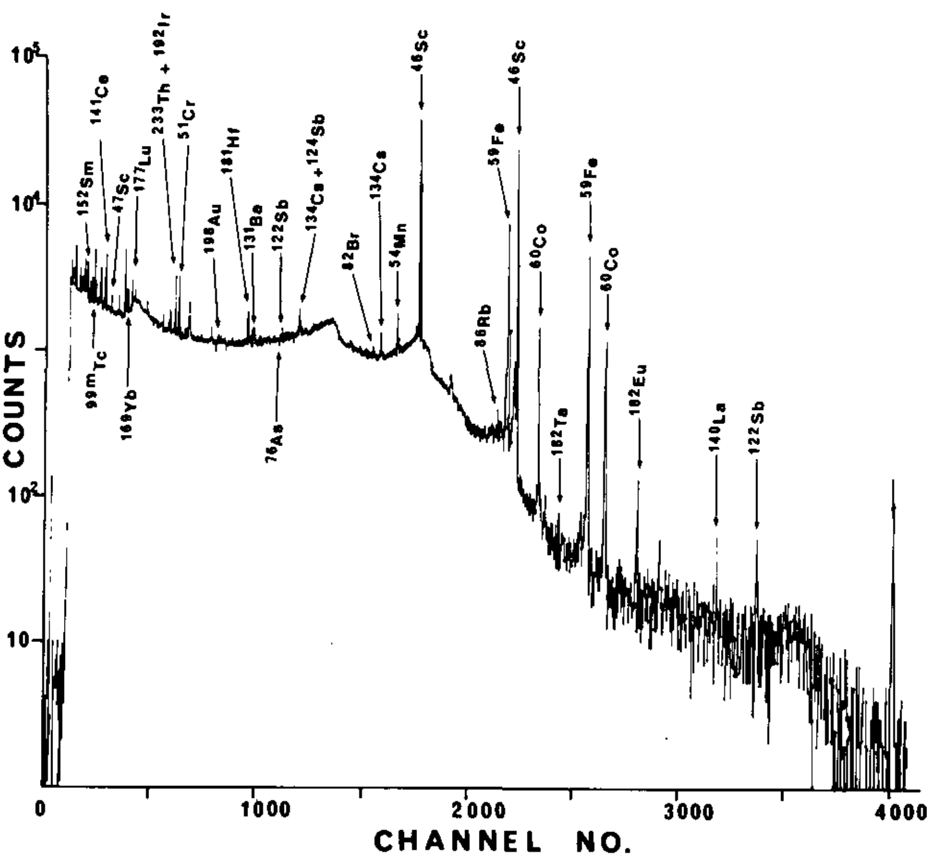


Fig 1. γ-ray spectrum of Pond Sediment.
sample wt., *ca.* 300 mg; irradiation station, Ph-2;
irradiation time, 1 hr; cooling time, *ca.* 18 days.
device, NAIG 4K channel MCA equipped with the
Ge(Li) detector (ORTEC, 53 cc); counting time, 2000 sec.

e. Data treatment

The programmes named COVIDN and GAMMA, both of which were developed by the authors, were used to find peaks, calculate peak areas, identify nuclides and finally give concentrations by normalizing cooling periods, detector efficiencies, nuclear constants and neutron spectrum with which samples and standards were irradiated. COVIDN calculates peak areas in a similar manner to a manual calculation and GAMMA does it by fitting peaks to a Gaussian function plus an exponential with a base line of quadratic form.

f. Nuclear data

In Table III, nuclear data on some of the nuclides used for checking the method are presented.

Results and Discussion

a. Application of the neutron spectrum monitor method to standard samples

Representative elements which have different sensitivities to the flux ratio were examined at various irradiation stations. The comparison of amounts taken with those calculated is presented in Table IV. Although neutron spectra are considerably different, fairly good agreements are obtained. It is more important that the values determined at the different irradiation stations are consistent except in a few cases. The data in parentheses for Lu in Table IV are not corrected for the neutron temperature. The calculation of g values by Eq. (15) revealed that the neutron temperatures of pneumatic facilities were 80-85 ℃ which were in good agreement with 'nominal' values.

b. Analytical results for geological reference materials

In Table V, the analytical values for JG-1 (Geological Survey of Japan) and Pond Sediment obtained by NAA and XRF are given. In the case of JG-1, the Geological Survey of Japan (GSJ) has been compiling the data obtained by different analytical techniques and provided by researchers of different disciplines[11]. Therefore, the recommended values by GSJ and the ranges of the reported values are cited for reference. Reasonably good agreements are obtained for most of the elements in JG-1 except for cobalt. Since cobalt is one of the elements which can be easily and accurately determined by neutron activation analysis, the values for cobalt determined by the present work may be more accurate than the average value reported. Chromium concentrations in JG-1 determined by neutron activation analysis are sometimes twice as much as the recommended value. Contamination of

Table III

Nuclear Data Used in the Present Work

Element	Nuclide	Isotopic Abundance	$T_{1/2}$	E (keV)	Branching Ratio	σ_0	I'
Sc	^{46}Sc	1.00	84.0d	889.2	1.00	26.5	0
				1120.6	1.00		
Fe	^{59}Fe	0.0031	44.6d	142.4*	0.0085	1.13	0.65
				192.2	0.028		
				1099.3	0.565		
				1291.6	0.432		
Co	^{60}Co	1.00	5.27y	1173.2	1.00	37.0	50
				1332.5	1.00		
Br	^{82}Br	0.493	35.34h	554.3	0.726	26.9	92
				776.5	0.835		
				1044.0	0.271		
				1317.4	0.265		
Mo	^{99}Mo	0.244	60.0h	181.0	0.070	0.130	7.5
				739.7	0.120		
				778.2	0.048		
	^{99m}Tc		6.07h	140.3	0.900		
Sb	^{122}Sb		2.68d	564.1	0.630	6.25	180
				692.8	0.327		
				1256.8	0.0065		
	^{124}Sb		60.3d	602.7*	0.980	4.32	120
				645.8*	0.071		
				722.8*	0.106		
				1691.0*	0.457		
Cs	^{134}Cs	1.00	2.046y	604.6	0.980	29.0	450
				795.8	0.880		
La	^{140}La	0.991	40.22h	328.7	0.216	8.20	7.5
				487.0	0.465		
				1596.2	0.965		
Yb	^{169}Yb	0.0014	30.7d	177.2	0.220	3470	23500
				198.0	0.35		
				307.7	0.100		
Lu	^{177}Lu	0.026	6.71d	113.0*	0.066	2100	1478
				208.0	0.111		
W	^{187}W	0.386	27.8h	479.5	0.260	37.8	420
				567.8	0.200		
				685.7	0.320		
Au	^{198}Au	1.00	2.697d	411.8	0.950	98.8	1505
U	^{238}U	0.99276	2.350d	228.2*	0.120	2.74	280
				277.6	0.140		

* γ-rays marked were not used because either their branching ratios are inaccurate or they likely to suffer hindrances by other nuclides.

Table IV

Determination of Standard Samples by Multiflux Monitor Method

Element	Added (μg)	Determined values at irradiation positions				
		pn-1 (μg)	pn-2 (μg)	pn-3 (μg)	hydr. (μg)	E-2 (μg)
Au	15.9	15.9	15.6	17.4	15.8	15.5
Br	100	104	109	99	103	–
La	100	97	97	88	92	81
U	11.0	10.7	10.7	10.7	10.8	11.4
Hf	100	98	101	101	94	98
W	100	92	–	94	94	107
Fe	30.0mg	30.7	30.6	30.0	30.2	29.6
Cs	100	90	90	95	90	–
Cr	100	–	96	98	98	–
Yb	100	94	94	92	94	80
Mo	1000	1040	1165	1070	1062	1053
Sc	10.0	11.8	12.6	11.8	11.3	11.9
Lu	100	(213)	(209)	(207)	(226)	(181)
		102	99.5	98.6	102	91.7
		80°C	80°C	80°C	100°C	60°C
						97.8
						40°C

the element during the sample preparation and irradiation is very unlikely, because blank runs so far examined have never exhibited significant amounts of those elements listed in Table V. The reason for this discrepancy is not clear.

The concentrations of the elements listed for Pond Sediment are corrected for the water content (11 %) which was measured independently by drying samples at 110 °C for 4 hrs. Good reproducibility for the analytical data of the material suggests that Pond Sediment is homogeneous enough to be used as a certified reference material.

Table V

Neutron Activation and X-ray Fluorescence Analysis of JG-1 and Pond Sediment

			JG-1				
Element	Nuclide	γ-ray (keV)	Determined Content	Agerage	Reported Range	Pond Sediment Content	Method
				Values in %		Values in %	
Fe	Fe-59	1099.0	1.45±0.05 (9)	1.53	1.36–1.76	6.41±0.12 (10)	NAA
Na	Na-24	1368.6	2.46±0.11 (5)	2.51	2.33–2.66	0.541±0.014 (10)	NAA
K						0.720±0.018 (15)	XRF
Ca						0.624±0.011 (14)	XRF
Ti						0.678±0.013 (15)	XRF
				Values in μg/g		Values in μg/g	
Sm	Sm-153	103.18	5.60±0.4 (7)	4.6	4.15–5.6	5.21±0.14 (9)	NAA
Ce	Ce-141	145.43	55±6 (9)	43.2	41.9–47	41.5±1.6 (10)	NAA
Lu	Lu-177	208.34	0.64±0.08 (7)	0.36	0.22–0.52	0.46±0.02 (10)	NAA
U	Np-239	277.63	3.53±0.18 (5)	3.3	2–4.67	1.67±0.25 (10)	NAA
Th	Pa-233	311.98	14.5±1.20 (5)	13.5	11.5–15.6	5.81±0.27 (10)	NAA
Cr	Cr-51	320.07	69.7±20.0 (5)	52.7	31–64	74.7±3.8 (10)	NAA
Hf	Hf-181	482.0	3.59±0.25 (9)	3.3	3.1–3.8	3.57±0.31 (10)	NAA
Yb	Yb-169	197.95	3.08±0.40 (7)	–	1.45–2.5	2.15±0.19 (10)	NAA
Au	Au-198	411.8	–	–	–	0.09±0.01 (10)	NAA
Ba	Ba-131	496.23	508±60 (5)	462	430–603	326±56 (10)	NAA
Sb	Sb-122	564.10	0.66±1.20 (3)	–	0.1–2.0	2.37±0.12 (10)	NAA
As	As-76	559.1	–	–	–	10.6±1.0 (10)	NAA
Br	Br-82	776.5	–	–	–	15.4±0.7 (5)	NAA
Cs	Cs-134	795.76	10.3±0.50 (5)	10.1	9.3–10.6	3.90±0.42 (10)	NAA
Mn	Mn-56	846.6	489±13 (3)	472	433–557	792±8 (5)	NAA
Sc	Sc-46	889.25	6.36±0.26 (9)	–	6.44–8.0	26.5±0.4 (10)	NAA
Rb	Rb-86	1078.80	192±15 (5)	181.3	171–202	48.1±5.9 (10)	NAA
Co	Co-60	1173.21	3.05±0.30 (9)	6.4	2–28	26.8±0.9 (10)	NAA
Ta	Ta-182	1221.38	–	–	–	[0.4]	NAA
Eu	Eu-152	1408.02	0.46±0.03 (7)	0.69	0.62–0.75	0.90±0.06 (10)	NAA
La	La-140	1596.40	23.2±1.9 (7)	22.1	18–22.5	18.1±0.6 (10)	NAA
Ni						31±3 (10)	XRF
Cu						238±2 (10)	XRF
Zn						382±6 (10)	XRF
Sr						114±2 (10)	XRF
Pb						119±1 (10)	XRF

NAA: Neutron activation analysis, XRF: X-ray fluorescence analysis

( ) : Number of determinations, [ ] : Rough estimation

The contents of Pond Sediment are based on the material dried at 110 ℃ for 4 hrs.

X-ray fluorescece Analysis (XRF) of Pond Sediment

a. Instrumentation

An energy-dispersive X-ray fluorescence spectrometer (ORTEC, Model TEFA-6111) equipped with a PDP-11/05 computer was used for the elemental analysis of Pond Sediment. A spectrum analysis was performed with a SEEK program (developed by ORTEC) which includes background subtraction, peak searching, and Gaussian peak fitting. The measurement conditions of the X-ray fluorescence spectrometer are shown in Table VI.

Table VI. X-ray fluorescence spectrometer conditions

Target:	Mo
Voltage:	50 KV
Current:	50 μA
Filter:	Mo
X-ray path:	Air
Counting time:	4000-8000 sec.

b. Standards for elemental analysis

A series of artificial reference standards were prepared by adding known amounts of the desired elements to dried (110℃, 4 hrs) anhydrous sedimentary silicates and by mixing in an agate ball-mill for 1 hour. The concentration ranges of the elements in the calibration standards were as follows; K: 5-25, Ca: 10-50, Ti: 1-5, Mn: 0.5-2.5, Fe: 20-100, Ni: 0.01-0.05, Cu: 0.02-0.10, Zn: 0.1-0.5, Pb: 0.01-0.05, As: 0.01-0.05, Rb: 0.05-0.25, Sr: 0.1-0.5 mg/g. Appropriate amounts of all the elements, the range of which is mentioned above, were added to each calibration standard.

c. Sample preparation

The standards and samples were dried in an oven at 110℃ for 4 hrs before analysis. Fifty μl of the internal standard solution (Cs: 100 mg/ml, Se: 1 mg/ml) were added to 500 mg of the artificial reference standards and samples (Pond Sediment). After drying again at 110℃ for 4 hrs and mixing in an agate ball-mill for 30 min, the analysis based on the direct measurement of powdered samples was performed. The analytical lines used were the $L\alpha_1$ for Pb and the $K\alpha_1$ for the other elements. The $L\alpha_1$ line of Cs was used as an internal standard for K, Ca, Ti, Mn and Fe, and the $K\alpha_1$ line of Se was chosen as an internal standard for Ni, Cu, Zn, As, Pb, Rb and Sr. Internal standardisation is preferable in order to compensate for instrumental and sample loading variations. The calibration curves were established by plotting the peak ratio, $I_x/I_{i.s.}$, where I_x and $I_{i.s.}$ are the peak intensities of the desired element and of the internal standard, respectively. In the case where soil or sediment samples are being analyzed, Fe or sometimes Mn, which are usually the major metallic elements in such samples, absorb X-rays of elements such as Ni, Cu and Zn. This matrix effect often results in underestimating the analytical values of Ni, Cu and Zn. Therefore, in the present work, the matrix effect correction was executed by referring to the content of Fe. The analytical values for Pond Sediment obtained by XRF are also included in Table V.

References

1) Fukai, R. and Meinke, W. W. (1959): *Nature*, 184, 815
2) Girardi, F., Guzzi, G. and Pauly, J. (1965): *Anal. Chem.*, 37, 1085
3) Alian, A., Born, H. J. and Kim, J. I. (1973): *J. Radioanal. Chem.*, 15, 535
4) Van der Linden. R., De Corte, F. and Hoste, J. (1974): *ibid.*, 20, 729
5) Schmidt, P. F. and McMillan, D. T. (1976): *Anal. Chem.*, 48, 1962
6) Westcott, C. H., Walker, W. H. and Alexander, T. L. (1958): *Intern. Conf. on Peaceful Uses of Atomic Energy*, Geneva, 16, 70
7) Kanda, K., Nanjo, T., Kobayashi, K., Nakagome, Y., Kozuka. T., Tsukaguchi, K., Kimura, I. and Shibata, T. (1969): *JURRI-TR-60, Technical Rept., Res. Reactor Inst. Kyoto Univ.*
8) Koyama, M. and Matsushita, R. (1980): *Bull. Inst. Chem. Res., Kyoto Univ.* 58, 235
9) Takamatsu, T., Kawashima, M. and Koyama, M. (1980): *ibid.*, 58, 285
10) Takamatsu, T. (1978): *Bunseki Kagaku*, 27, 193
11) Ando, A., Kurasawa, H., Ohmori, T. and Takeda, E. (1974): *Geochem. J.*, 8, 175

CHAPTER VII

The Certification of Pond Sediment

K. Okamoto

The reference material certified for elemental composition is indispensable to analytical methods if accuracy and precision are to be achieved and maintained. To meet the ever-increasing demand from the many areas of science and industry, government-supported bodies in a number of countries are actively involved in the issuance of various categories of CRMs. In Japan, the National Institute for Environmental Studies (NIES) recently instigated a CRM programme to serve the needs of environmental scientists and the botanical reference material, Pepperbush, was the first standard issued. Reports on the preparation, analysis and certification of Pepperbush CRM have been published[1-4]. The second CRM to be issued is a geological sample, Pond Sediment, the preparation and analysis of which are described in the previous chapters in this booklet. Other categories of environmental CRMs already prepared include chlorella, freeze-dried serum, hair and mussel and analysis is underway.

In this chapter, we shall outline the procedures taken to enable the certification of Pond Sediment. The initial stage of the certification process requires analytical data for the various elements to be obtained from independent and established analytical techniques. A collaborative study on the elemental analysis of Pond Sediment has been carried out with a number of Japanese scientists and the analytical data obtained by various analytical techniques are first presented.

The certification of elemental composition has been performed using analytical data obtained at NIES and by the collaborating laboratories. The criteria for certification of elemental composition, and the certification process for Pond Sediment are described. The certified and reference values for Pond Sediment are also listed.

1. Analytical Techniques Employed for Elemental Analysis of Pond Sediment

"There are essentially two modes of measurement leading to the certification process: 1) the direct or in-house mode and 2) the interlaboratory or consensus mode. Each of these modes has its own advantages and disadvantages. At the National Bureau of Standards (NBS, USA), over 90 % of the

CRMs are produced through the direct or in-house mode. The advantages are that both technical and managerial control is in the hands of a few well-qualified scientists and managers. However, extensive and up-to-date measurement methods using the most accurate instruments are costly and CRMs thus produced are likely to be expensive, but the most serious objection to this mode is that independent assessment of the work becomes difficult, if not economically prohibitive5)".

At most national and international standards organizations, the interlaboratory mode has been used for certification. This mode has an advantage that through a series of laboratories an evaluation of analytical methods and characterization of the overall uncertainties of the methods can be obtained since information on within and between laboratory precision is available. However, our experience has shown that a danger which exists in using the interlaboratory mode is that the overall uncertainty for the properties under measurement very often becomes much larger than the range accepted for certification. Cali5) stressed, in the interlaboratory mode, that it is indispensable to know the quality of the participating laboratories and to insist on the use of a prior CRM as the unknown in order to be able to assure the laboratory's work is under control.

At NIES the analytical techniques currently available are limited so that analyses of Pond Sediment have been performed in the interlaboratory mode using various analytical techniques at 31 laboratories. The analytical techniques used for the elements in Pond Sediment are summarized in Table I. At NIES, atomic absorption spectrometry (AAS), flame emission spectrometry (FES), inductively coupled plasma emission spectrometry (ICP), X-ray fluorescence spectrometry (XRF), and spectrophotometry (SP) have been employed. Analytical results by the above techniques and by isotope dilution mass spectrometry (IDMS), instrumental neutron activation analysis (INAA), instrumental photon activation analysis (IPAA), spectrofluorimetry (SF), gravimetry (Grav), potentiometry (Pot) and volumetric analysis (Vol) have also been provided by collaborating laboratories. More than 50 elements in Pond Sediment have been determined by 12 independent analytical techniques.

2. *Cooperating Laboratories*

Table II indicates the principal investigators, addresses, and code numbers for the collaborating laboratories, including members of staff of NIES. Most of the collaborating participants are members of the research group on CRMs under the chairmanship of Professor T. Kiba (Kanazawa Institute of Technology) and had previous experience in analyzing NBS River Sediment standard reference material.

Table I

Analytical Techniques Used for Elements

Analytical Technique	Element
Atomic absorption spectrometry (AAS)	As, Ca, Cd, Co, Cr, Cu, Fe Hg, K, Mg, Mn, Na, Ni, Pb Rb, Sb, Sn, Tl, Zn
Flame emission spectrometry (FES)	K, Na, Rb
Inductively coupled plasma emission spectrometry (ICP)	Al, Ba, Be, Ca, Cd, Co, Cr Cu, Fe, K, Li, Mg, Mn, Na Ni, P, Pb, Sc, Si, Sr, Ti, V Y, Zn, Zr
X-ray fluorescence spectrometry (XRF)	Br, Ca, Cu, Fe, K, Mn, Ni Pb, Rb, Sr, Ti, Zn
Isotope dilution mass spectrometry (IDMS)	Ag, Ba, Cd, Cu, Pb, Rb, Sr Tl
Instrumental neutron activation analysis (INAA)	Al, As, Au, Ba, Br, Ca, Ce Co, Cr, Cs, Cu, Eu, Fe, Hf In, K, La, Lu, Mg, Mn, Na Rb, Sb, Sc, Se, Sm, Sr, Ta Tb, Th, Ti, U, V, W, Yb Zn, Zr
Instrumental photon activation analysis (IPAA)	As, Ca, Co, Cs, Fe, Mg, Mn Na, Ni, Pb, Rb, Sb, Sr, Ti Y, Zr
Spectrophotometry (SP)	Al, As, Cr, Fe, Mn, P, Sb Ti
Spectrofluorimetry (SF)	Eu, Se, Sm
Gravimetry (Grav)	Al, Ca, Si
Volumetric analysis (Vol)	Al, Ca, Fe, Mg
Potentiometry (Pot)	Br, Cl, F

Table II Names and Affiliations of Collaborating Analysts

Laboratory Code	Principal Investigator	Affiliation
01	K. Okamoto	National Institute for Environmental Studies, Chemistry & Physics Division, Ibaraki 305.
02	T. Takamatsu	*ibid.* ,Water & Soil Division, Ibaraki 305.
03	M. Koyama	Kyoto Univ., Research Reactor Inst., Div. of Hot Lab., Kumatori-cho, Sennan-gun, Osaka 590-04.
04	H. Akaiwa	Gunma Univ., Dept. of Chemistry, Kiryu, Gunma 376.
05	M. Ambe	Sagami Chemical Research Centre, Nishi-Ohnuma, 4-4-1, Sagamihara-shi, Kanagawa 229.
06	M. Ichikuni	Tokyo Inst. of Technology, Dept. of Envir. Chem. & Eng., Nagatsuka, Midori-ku,Yokohama 227.
07	S. Iwata	Kyoto Univ., Research Reactor Inst., Div. of Hot Lab., Kumatori-cho, Sennan-gun, Osaka 590-04.
08	M. Kamada	Kagoshima Univ., Chemical Inst., Koorimoto, 1-21-35, Kagoshima 890.
09	K. Kimura	Aoyama Gakuin Univ., College of Sci. & Tech., 16-1, Chitosedai 6, Setagaya, Tokyo 157.
10	N. Suzuki	Tohoku Univ., Dept. of Chemistry, Aoba, Sendai 980.
11	T. Sotobayashi	Niigata Univ., Dept. of Chemistry, Igarashi, Niigata 950-21.
12	Y. Takashima	Kyushu Univ., Dept. of Chemistry, Hakozaki, Higashiku, Fukuoka 812.
13	K. Terada	Kanazawa Univ., Dept. of Chemistry, Marunouchi, 1-1, Kanazawa 812.
14	K. Nagashima	Univ. of Tsukuba, Dept. of Chemistry, Sakura-mura, Ibaraki 305.
15	S. Nagatsuka	Tokyo Metropolitan Isotope Research Centre, 2-11-1, Fukazawa, Setagaya-ku, Tokyo 158.
16	Y. Nishikawa	Kinki Univ., Dept. of Chemistry, Kowakae, Higashi-Osaka, Osaka 577.
17	Y. Hashimoto	Keio Univ., Dept. of Applied Chemistry, Hiyoshi, Kohoku-ku, Yokohama 223.
18	H. Hamaguchi	Japan Chemical Analysis Centre, 295-3, Sanno-cho, Chiba-shi, Chiba 281.
19	M. Furukawa	Nagoya Univ., Dept. of Chemistry, Nagoya, Aichi 464.
20	Y. Murakami	Kitasato Univ., School of Hygienic Science, 1-15-1, Kitasato, Sagamihara-shi, 228.
21	M. Murozumi	Muroran Inst. of Technology, Dept. of Applied Chemistry, Mizumoto-cho, 27-1, Muroran-shi 050.
22	N. Yamagata	Inst. of Public Health, Dept. of Rediological Health, 6-1, Shiroganedai, 4, Minato-ku, Tokyo 108.
23	K. Watanuki	Tokyo Univ., College of General Education, Dept. of Chem., Komaba, 3-8-1, Meguro-ku, 153.
24	K. Kudo	Ibaraki Electrical Comm, Lab., Nippon Telegraph & Telephone Public Corp., Tokai, Ibaraki 319-11.
25	H. Haraguchi	Tokyo Univ., Dept. of Chemistry, Hongo 7-3-1, Bunkyo-ku, Tokyo 113.
26	S. Toda	Tokyo Univ., Dept. of Agric. Chemistry, Yayoi 1-1-1, Bunkyo-ku, Tokyo, 113.
27	E. Tsuchiya	Tokyo Metropolitan Res. Lab. of Public Health, Hyakunin-cho, 3-24-1, Shinjuku-ku, Tokyo 160.
28	K. Nozu	Univ. of Tsukuba, Chemical Analysis Center, Sakura-mura, Ibaraki 305.
29	H. Takagi	Kanagawa Prefectural Public Health Lab., Nakao-cho, Asahi-ku, Yokohama 241.
30	Y. Takahashi	Tokyo Metropolitan Res. Inst. for Environ. Protection, Yurakucho, 2-7-1, Chiyoda-ku, Tokyo 100.
31	K. Yamagaki	Niigata City Water Works Bureau, Aoyama, 1283-6, Niigata 950-21.
32	V. Luciano	Fisher Scientific Co., Jarrell-Ash Div., 590 Lincoln St., Waltham. Mass, 02154, U.S.A.

3. Analytical Values for Pond Sediment

Table III compiles the analytical values for Pond Sediment, the analytical techniques employed and the code number of the collaborating participants.

The analytical procedures employed at NIES and those for INAA have been reported in detail in Chapter III-VI. The cooperating laboratories were requested to perform determinations for elements which they considered they were equipped to do. The results received from the participating laboratories were normalized whenever necessary, for example, to the appropriate units. In compiling the data the following procedures were adopted.

(1) All values given in Tabel III were taken from the original reports of the participants with as little change as possible; significant figures of the values given in the Table are identical to those of the data reported by the participants.

(2) Data which were reported based on "silica-gel" dry weight were normalized to that based on drying in an air-oven at 110℃ for 4 hrs (mean moisture loss, 11 %).

(3) When a laboratory employed two or more independent analytical techniques for the same elements, the mean value produced by each technique was treated and presented separately.

(4) Disregarding differences in detailed procedures existing among individual laboratories which used the same method, the averages of the values obtained by each technique were calculated.

4. Certification of Pond Sediment

"The term reference material is used to describe a generic class of well-characterized, stable, homogeneous material, produced in quantity and having one or more physical or chemical properties experimentally determined within stated measurement uncertainties"[6]. In the preparation and certification of each reference material, therefore, it must be assured that the material is uniform and stable, and that test methods provide repeatable and consistent results. Reference materials are certified using the data obtained by accurate and reliable analytical techniques and, eventually, the properties certified are condensed into the form presented on the certificate, where the numerical values are expressed into two parts: the certified value of the property and uncertainty of this value.

Here we need to consider the reliability of analytical results which is a function of accuracy and precision (reproducibility). The precision of results in terms of the standard deviation can readily be determined for analytical methods by internal measurements. The determination of accuracy is, however, no easy task and the evaluation of each analytical method with

Table III

Analytical Values(μg/g) for Pond Sediment

Element	Value†(μg/g)	Technique	Laboratory Code
Ag	0.883	IDMS	21
Al	10.7(Wt.%)	ICP	01
	9.27	INAA	07
	9.39	INAA	07
	10.3	INAA	09
	9.77	GRAV	09
	10.5	ICP	14
	10.7	INAA	15
	10.6	SP	16
	10.5	INAA	17
	11.04	INAA	18
	10.08	INAA	19
	10.4	INAA	20
	9.41	VOL	23
	9.2	ICP	28
	10.44	ICP	32
As	11.5	AAS	01
	10.6	INAA	03
	11.6	SP	08
	12.9	IPAA	10
	13	INAA	15
	13.0	INAA	17
	10.4	INAA	18
	12.6	INAA	19
	11.3	INAA	20
	13.5	INAA	22
	13	INAA	24
	10.3	INAA	29
Au	0.090	INAA	03
	0.089	INAA	24
Ba	335	ICP	01
	326	INAA	03
	343	INAA	07
	294	INAA	12
	330	INAA	15
	650	INAA	18
	355	INAA	19
	309	IDMS	21
	308	ICP	32

Element	Value†(μg/g)	Technique	Laboratory Code
Be	2.3	ICP	01
Br	17.5	XRF	01
	15.4	INAA	03
	15	POT	04
	17.2	INAA	15
	17.7	INAA	18
	16.7	INAA	19
	17.1	INAA	20
	16	INAA	24
C	5.53(Wt.%)	*	05
	5.36	*	12
	5.44	*	14
	5.28	*	16
	5.43	*	17
	5.2	*	22
Ca	0.84(Wt.%)	AAS	01
	0.82	ICP	01
	0.624	XRF	02
	0.95	VOL	04
	0.876	IPAA	10
	0.81	AAS	12
	0.80	ICP	14
	0.82	INAA	15
	0.88	INAA	17
	0.80	INAA	19
	0.81	AAS	23
	0.76	GRAV	25
	0.72	ICP	28
	0.80	ICP	32
Cd	0.83	AAS	01
	0.81	ICP	01
	0.79	AAS	08
	0.824	IDMS	21
	0.90	AAS	30
Ce	41.5	INAA	03
	40.0	INAA	07
	38.7	INAA	07
	37.1	INAA	12
	47.8	INAA	15
	45	INAA	17

Element	Value† (μg/g)	Technique	Laboratory Code
Ce	39.3	INAA	18
	26	INAA	20
	39.1	INAA	22
	36.5	INAA	29
Cl	85	POT	04
Co	27.8	ICP	01
	29.4	AAS	01
	26.8	INAA	03
	25	AAS	04
	28.0	INAA	07
	25.1	INAA	07
	29.2	IPAA	10
	27.7	INAA	12
	23.1	AAS	13
	27.6	INAA	15
	29	INAA	17
	28.1	INAA	18
	25.1	INAA	19
	28	INAA	20
	26.9	INAA	22
	25.3	INAA	24
	26.2	AAS	25
	25.7	AAS	27
	28	ICP	28
	26.1	INAA	29
	28.3	ICP	32
Cr	73.3	SP	01
	67.7	ICP	01
	62.4	AAS	01
	74.7	INAA	03
	69.5	INAA	07
	57.3	INAA	12
	44	ICP	14
	68	INAA	15
	63.9	SP	16
	82	INAA	17
	76	INAA	18
	76.5	INAA	19
	75	INAA	20
	87.0	INAA	22
	76	INAA	24
	77.4	INAA	29
	78	SP	30
	74.3	ICP	31
	54.7	ICP	32

Element	Value†(μg/g)	Technique	Laboratory Code
Cs	3.90	INAA	03
	2.9	INAA	07
	3.3	IPAA	10
	2.64	INAA	12
	3.7	INAA	15
	4.7	INAA	17
	4.54	INAA	18
	3.57	INAA	19
	3.4	INAA	20
Cu	210	AAS	01
	220	ICP	01
	238	XRF	02
	203	AAS	04
	214		05
	216	AAS	06
	209	AAS	08
	200	AAS	11
	203	AAS	13
	134	ICP	14
	200	AAS	16
	260	INAA	17
	210	AAS	18
	210	IDMS	21
	260	INAA	24
	220	AAS	25
	215	AAS	27
	186	AAS	30
	205	ICP	31
	199	ICP	32
Eu	0.90	INAA	03
	1.18	INAA	07
	1.14	INAA	07
	1.22	INAA	12
	1.5	INAA	15
	1.10	SF	16
	1.0	INAA	17
	1.26	INAA	18
	1.22	INAA	19
	1.45	INAA	22
	1.25	INAA	24
F	283	POT	25

Element	Value†(μg/g)	Technique	Laboratory Code
Fe	6.62(Wt.%)	ICP	01
	6.43	AAS	01
	6.30	XRF	02
	6.41	INAA	03
	6.52	SP	04
	6.47	AAS	06
	6.37	INAA	07
	5.98	INAA	07
	6.78	INAA	09
	7.01	AAS	09
	6.47	IPAA	10
	6.25	AAS	11
	6.68	INAA	12
	6.32	AAS	13
	6.98	ICP	14
	6.9	INAA	15
	6.05	SP	16
	7.2	INAA	17
	6.70	INAA	18
	6.04	AAS	18
	6.28	INAA	19
	6.7	INAA	20
	6.58	INAA	22
	6.16	VOL	23
	6.7	INAA	24
	6.70	SP	25
	6.31	AAS	27
	6.6	ICP	28
	6.91	INAA	29
	6.37	ICP	31
	6.68	ICP	32
H	1.77(Wt.%)	*	05
	1.29	*	12
	1.63	*	14
	1.97	*	16
	1.52	*	17
Hf	3.57	INAA	03
	3.44	INAA	07
	2.94	INAA	07
	3.3	INAA	09
	3.14	INAA	12
	4.4	INAA	17
	3.90	INAA	18

Element	Value†(μg/g)	Technique	Laboratory Code
Hg	1.42	AAS	01
	1.33	AAS	05
	1.24	AAS	08
	1.38	AAS	12
	1.46	AAS	22
	1.3	AAS	26
In	0.23	INAA	20
K	0.678(Wt.%)	AAS	01
	0.692	FES	01
	0.720	XRF	02
	0.71	FES	04
	0.693	AAS	06
	0.58	INAA	07
	0.63	INAA	07
	0.77	INAA	09
	0.66	AAS	11
	0.78	FES	12
	0.70	FES	13
	0.64	ICP	14
	0.68	INAA	15
	0.64	INAA	17
	0.72	INAA	18
	0.592	INAA	19
	0.58	INAA	20
	0.78	INAA	22
	0.75	AAS	23
	0.622	INAA	24
	0.76	FES	25
	0.60	ICP	28
	0.71	ICP	32
La	18.1	INAA	03
	15.1	INAA	07
	13.2	INAA	07
	16.8	INAA	09
	16.1	INAA	12
	21.5	INAA	15
	18	INAA	17
	17.4	INAA	18
	16.3	INAA	19
	21.8	INAA	20
	16.9	INAA	22
	15.4	INAA	29
Li	22	ICP	28
	17.1	ICP	32

Element	Value†(μg/g)	Technique	Laboratory Code
Lu	0.46	INAA	03
	0.55	INAA	17
	0.47	INAA	18
Mg	0.925(Wt.%)	ICP	01
	0.785	AAS	01
	0.76	AAS	04
	0.76	VOL	04
	0.796	AAS	06
	1.04	AAS	09
	0.82	AAS	09
	1.01	AAS	09
	1.00	IPAA	10
	0.74	AAS	11
	0.85	AAS	12
	0.79	AAS	13
	0.79	AAS	16
	0.59	AAS	18
	0.70	INAA	20
	0.78	AAS	23
	0.68	ICP	28
	0.80	ICP	32
Mn	798	ICP	01
	774	AAS	01
	681	XRF	02
	792	INAA	03
	740	AAS	04
	834	AAS	06
	841	INAA	07
	753	INAA	07
	860	INAA	09
	889	IPAA	10
	860	AAS	12
	722	AAS	13
	750	ICP	14
	700	INAA	15
	756	AAS	16
	830	INAA	17
	733	INAA	18
	697	AAS	18
	760	INAA	19
	863	INAA	20
	700	INAA	24
	769	SP	25
	572	AAS	27
	670	ICP	28

Element	Value†(μg/g)	Technique	Laboratory Code
Mn	722	ICP	31
	790	ICP	32
N	0.44(Wt.%)	*	05
	0.45	*	12
	0.42	*	14
	0.38	*	16
	0.45	*	17
	0.44	*	22
Na	0.534(Wt.%)	AAS	01
	0.562	FES	01
	0.541	INAA	03
	0.60	FES	04
	0.508	AAS	06
	0.567	INAA	07
	0.537	INAA	07
	0.61	INAA	09
	0.629	IPAA	10
	0.60	INAA	12
	0.59	FES	13
	0.54	INAA	15
	0.58	INAA	17
	0.60	INAA	17
	0.588	INAA	18
	0.55	INAA	19
	0.59	INAA	20
	0.598	INAA	22
	0.47	INAA	24
	0.65	FES	25
	0.43	ICP	32
Ni	41.8	ICP	01
	35.8	AAS	01
	31	XRE	02
	31	AAS	04
	39.6	IPAA	10
	40.7	AAS	13
	38.2	AAS	25
	41	ICP	28
	39	AAS	30
	30.1	ICP	32
P	0.143(Wt.%)	ICP	01
	0.14	SP	05
	0.12	ICP	14
	0.14	ICP	28
	0.139	ICP	31
	0.12	ICP	32

Element	Value†(μg/g)	Technique	Laboratory Code
Pb	110	ICP	01
	107	AAS	01
	119	XRF	02
	104	AAS	04
	103	AAS	08
	108	IPAA	10
	98	AAS	11
	103	AAS	13
	82	ICP	14
	105	IDMS	21
	103	AAS	25
	106	AAS	27
	105	AAS	30
Rb	43.9	AAS	01
	43.4	FES	01
	50	XRF	02
	48.1	INAA	03
	37.4	INAA	07
	40.5	INAA	07
	45.0	IPAA	10
	48	INAA	15
	50	INAA	18
	46.2	INAA	19
	37	INAA	20
	41.8	IDMS	21
Sb	2.37	INAA	03
	2.3	INAA	07
	1.8	SP	08
	2.1	IPAA	10
	2.12	AAS	11
	3.5	AAS	13
	2.4	INAA	15
	1.54	AAS	17
	2.4	INAA	17
	2.17	INAA	18
	2.17	INAA	19
	2.31	INAA	20
	1.67	INAA	24
	1.66	INAA	29
Sc	27.6	ICP	01
	26.5	INAA	03
	27.0	INAA	07
	24.9	INAA	07
	26.2	INAA	09
	28.3	INAA	12

Element	Value†(μg/g)	Technique	Laboratory Code
Sc	25	ICP	14
	30.4	INAA	15
	30	INAA	17
	30.9	INAA	18
	28.2	INAA	19
	27	INAA	20
	29	INAA	22
	36	INAA	24
	20	ICP	28
Se	0.50	INAA	12
	0.576	SF	16
SiO_2	44.5(Wt.%)	GRAV	04
	45.99	GRAV	06
	45.85	GRAV	09
	46.33	GRAV	23
	45.70	GRAV	25
	48.4	ICP	31
	43.93	ICP	32
Sm	5.21	INAA	03
	5.39	INAA	15
	5.03	SF	16
	4.2	INAA	17
	5.72	INAA	18
	4.40	INAA	19
	5.37	INAA	22
	5.50	INAA	29
Sn	12.6	AAS	13
Sr	107	ICP	01
	114	XRF	02
	116	IPAA	10
	130	INAA	12
	95	ICP	14
	108	IDMS	21
	76	ICP	28
	103	ICP	32
Ta	0.93	INAA	12
	0.51	INAA	18
Tb	0.23	INAA	07
	0.39	INAA	07
	0.41	INAA	12
	0.78	INAA	18

Element	Value† (μg/g)	Technique	Laboratory Code
Th	5.81	INAA	03
	3.63	INAA	07
	2.9	INAA	07
	5.25	INAA	12
	4.9	INAA	17
	5.52	INAA	18
	4.6	INAA	20
	5.5	INAA	22
Ti	0.62(Wt.%)	ICP	01
	0.678	XRF	02
	0.38	INAA	07
	0.77	INAA	09
	0.619	IPAA	10
	0.59	INAA	15
	0.58	INAA	17
	0.71	INAA	18
	0.70	INAA	20
	0.607	SP	25
	0.61	ICP	28
	0.59	ICP	32
Tl	0.31	AAS	11
	0.468	IDMS	21
U	1.67	INAA	03
	1.17	IDA	11
	1.8	INAA	18
V	254	ICP	01
	219	INAA	07
	199	INAA	07
	240	INAA	15
	250	INAA	17
	240	INAA	18
	265	INAA	19
	255	INAA	20
	280	ICP	28
	285	ICP	31
	228	ICP	32
W	2.5	INAA	18
Y	26.7	IPAA	10
	20	ICP	14
	21.0	ICP	32

Element	Value† (μg/g)	Technique	Laboratory Code
Yb	2.15	INAA	03
	2.12	INAA	12
	2.92	INAA	18
	2.6	INAA	24
Zn	348	ICP	01
	343	AAS	01
	382	XRF	02
	347	AAS	04
	356	AAS	06
	344	AAS	08
	331	AAS	11
	300	AAS	12
	338	AAS	13
	360	INAA	17
	337	INAA	18
	338	AAS	18
	340	INAA	19
	360	INAA	24
	360	AAS	25
	340	ICP	25
	329	AAS	27
	290	ICP	28
	342	ICP	31
	306	ICP	32
Zr	132	INAA	09
	131	IPAA	10
	113	ICP	14
	102	ICP	32
Ignition Loss	16.8(Wt.%)	GRAV	05
	17.96	GRAV	09
	17.0	GRAV	13
	16.9	GRAV	14
	18.33	GRAV	16
	17.5	GRAV	21
	18.50	GRAV	23
	17.88	GRAV	25

† based on dry weight (at 110 °C for 4 hrs in an air-oven).

* CHN analyser.

respect to their inherent accuracy is indispensable if certification is to be achieved. On the basis of pure statistical considerations it is difficult to judge which value is closest to the "true value".

At NBS, analytical methods are classified considering their accuracy into the following categories: (1) definitive method, (2) reference method, (3) field method. "A definitive method is one in which all major significant parameters have been related by direct or a solid chain of evidence to the base or derived units of the SI (International System of Units)"7). At NBS, isotope dilution mass spectrometry (IDMS) has been extensively used as a definitive method for the accurate measurement of inorganic constituents at trace levels. The principle and inherently excellent accuracy of isotope dilution mass spectrometry have been described in several reports6-9) by NBS staff. At NIES a facility for IDMS is now under construction.

"A reference method is a method of proven accuracy. Here the accuracy of the method rests on or is demonstrated usually by (but not always) a definitive method. Reference methods are generally arrived at by consensus. That is, fairly extensive testing of the accuracy claims are made by a number of laboratories before its status is accepted by the measurement laboratories that will be using the method"7). The accuracy of a reference method can also be established through the use of a CRM(s) whose property(ies) has been accurately determined by a definitive method. Since reference methods require highly skilled scientists and moderately sophisticated instruments, they may not always be acceptable for routine field use where time and cost are important considerations.

The classification of analytical methods by NBS is reasonable and practically useful for the certification process. In other words the classification provides a viable approach to certification. The criteria used for certification of elemental composition of Pond Sediment, which correspond to those used at NBS, are as follows: (1) The first criterion is that analytical values should be determined "by a definitive method", for instance, IDMS and gravimetry. Two or more independent analyses by the definitive methods are, however, required. (2) The second criterion is "by two or more independent reference methods", for example, AAS and INAA.

Basically we employed both criteria for the certification of the elemental composition of Pond Sediment. However, the IDMS results provided have not completely satisfied the first item because the data represented replicates at one laboratory only. Also the elements determined by IDMS were limited owing to the principle and capability of the method. In order to certify the elemental composition of Pond Sediment, therefore, we adopted the values determined not only by IDMS but also by reference methods. For those elements where values were not determined by the definitive method, the analytical values determined by two or more reference methods were adopted for certification.

Table IV shows the elements and the analytical techniques used for analysis of Pond Sediment. The definitive method, that is IDMS, has been employed to determine Ag, Ba, Cd, Cu, Pb, Rb, Sr and Tl. Three or more independent reference methods have also been used for each element certified. Atomic absorption spectrometry has been used most frequently. Neutron activation analysis has been frequently used for multielement analysis while inductively coupled plasma emission spectrometry has been employed for simultaneous multielement analysis.

Table IV

Analytical Techniques and Elements Determined

MAJOR CONSTITUENTS	
Aluminium	ICP INAA SP Grav Vol
Iron	AAS ICP XRF INAA IPAA SP Vol
MINOR CONSTITUENTS	
Calcium	AAS ICP XRF INAA IPAA Grav Vol
Potassium	AAS FES ICP XRF INAA
Sodium	AAS FES INAA IPAA
TRACE CONSTITUENTS	
Zinc	AAS ICP XRF INAA
Copper	AAS ICP XRF IDMS INAA
Lead	AAS ICP XRF IDMS IPAA
Chromium	AAS ICP INAA SP
Nickel	AAS ICP XRF IPAA
Cobalt	AAS ICP INAA IPAA
Arsenic	AAS INAA IPAA SP
Cadmium	AAS ICP IDMS

Abbreviations used for analytical techniques are indicated in Table I

Next, we need to illustrate how the certification was performed. Let us consider lead. There were 13 independent analytical values for lead determined by AAS, ICP, IDMS, IPAA and XRF, as presented in Table III. Grubbs's or Pearson-Stephens's statistical outlier test[10,11]) was first applied to determine whether any results should be rejected. In the case of lead, both the lowest value (82 μg/g by ICP) and the highest value (119 μg/g by XRF) were suspected to be outliers so that Pearson-Stephens's outlier test was applied. Both values were judged to be outliers at the significance level of 5 %, thus the remaining 11 values for lead were used for further statistical treatment. Analytical problems associated with incomplete dissolution (ICP) and instrumental imprecision (XRF) were also suggested after consideration of analytical values for other elements provided by the respective methods. The entire range of lead values lies between 98 and 110 μg/g. The overall mean and standard deviation are computed to be 104.7 and 3.2 μg/g respectively, therefore, the overall mean ± 2 times the standard deviation is 105 ± 6 μg/g.

Here we need to explain how we estimated the uncertainties or the overall errors of the certified values. Uncertainty includes sample variability, measurement errors and possible bias among analytical methods. As mentioned in Chapter II, the homogeneity test for certain elements indicated that sample variability among bottles may be considered negligible. Therefore, we should consider measurement errors and systematic errors among methods.

Using the example of lead, the estimation of the accuracy and precision will be explained. Fig 1 shows the entire range (1), the overall mean ± 2 times the standard deviation (2), the 95 % confidence interval computed from the AAS results (3) which includes the variation within and between laboratories. The 95 % confidence intervals computed from IDMS (4), IPAA (5), and ICP (6) results obtained at one laboratory are also indicated in Fig 1.

Second, we should consider so-called possible bias or systematic error among analytical methods. In Fig 1, the center of the horizontal lines indicates the mean for each method. It is apparent that a small bias exists between the four methods (3) (4) (5) (6), though the overall mean (2) is almost identical to the mean obtained by IDMS. Just now, however, there is not enough data to estimate bias among the methods. One way is to use the mean obtained by the definitive method (IDMS) as the true value and then to estimate the accuracy of the other methods. As for the lead content of Pond Sediment, more independent results by IDMS could make this possible. In this case, the certified value for lead in Pond Sediment has been estimated to be 105 μg/g, based on the considerations of the mean obtained by IDMS and the overall mean of the 11 values. The uncertainty of the certified value has been estimated to be 6 µg/g based on 2 times the standard deviation of the 11 values and the 95 % confidence limits for the four methods.

The certified values for Pond Sediment are given in Table V and the criteria for certification were similar to that used in the case of lead, namely the certified values are based on consideration of the overall mean ± 2 times the standard deviation and the 95 % confidence limits of the various methods.

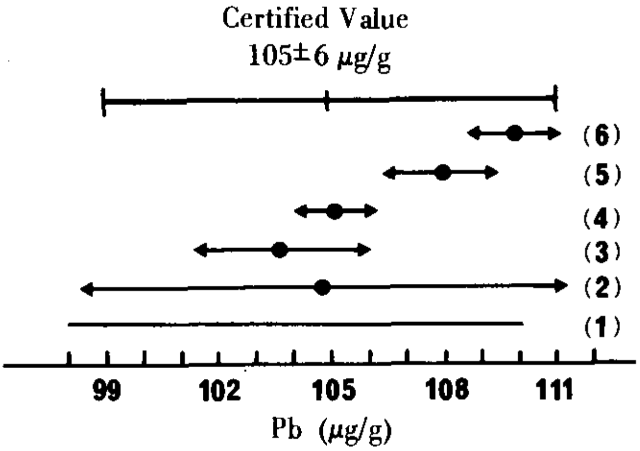


Fig 1. Summary of mean values and confidence intervals for lead by various analytical techniques

(1) Entire range of values reported (outliers are rejected).
(2) Mean ± 2-sigma (all values except for outliers)
(3) 95 % confidence interval for the mean (AAS)
(4) 95 % confidence interval for the mean (IDMS)
(5) 95 % confidence interval for the mean (IPAA)
(6) 95 % confidence interval for the mean (ICP)

Table V
Certified and Reference Values for Pond Sediment

Element	Content*
Certified Values	
MAJOR CONSTITUENTS	(Wt. Percent)
Aluminium	10.6±0.5
Iron	6.53±0.35
MINOR CONSTITUENTS	(Wt. Percent)
Calcium	0.81±0.06
Potassium	0.68±0.06
Sodium	0.57±0.04
TRACE CONSTITUENTS	(μg/g)
Zinc	343±17
Copper	210±12
Lead	105±6
Chromium	75±5
Nickel	40±3
Cobalt	27±3
Arsenic	12±2
Cadmium	0.82±0.06
Reference Values	
	(Wt. Percent)
Silicon	21
Titanium	0.64
Phosphorus	0.14
	(μg/g)
Manganese	770
Vanadium	250
Strontium	110
Rubidium	42
Scandium	28
Lanthanum	17
Bromine	17
Antimony	2.0
Mercury	1.3

*Dry weight basis: Sediment was dried in an air-oven at 110 °C for 4 hrs (mean moisture loss, approximately 11 %). The values represent a total analysis.

5. Reference Values for Pond Sediment

The reference values for Pond Sediment are also included in Table V. The reference values are defined as those values which were consistent but were obtained by only one reference method, or in the case of two or more reference methods used, if some analytical problems were suspected. For example, Hg was determined by only AAS, and La was determined by only INAA. Both these cases need more independent results. As for the other elements listed in Table V, the results by two or more independent analytical techniques were close, however, further examination of the sample dissolution procedure is required. We hope that with additional data reference values could resort to certified values at a later date.

References

1) Okamoto,K., Yamamoto,Y. & Fuwa,K. (1978): *Anal. Chem.*, 50, 1950
2) Okamoto,K. (ed): Preparation, Analysis and Certification of PEPPERBUSH Standard Reference Material, *NIES Research Report No. 18*
3) Okamoto,K. (1982): *Bunseki*, No. 5, 319
4) Okamoto,K. (1982): "Kankyo Bunseki no Shuho to Hyoka", Kiba T. *et al* (ed), p199-210, Tokyo Daigaku Shuppan Kai
5) Cali,J.P. (1980): "Production and Use of Reference Materials", Schmitt,B.F. (ed), p443-448, BAM, Berlin
6) Uriano,G.A. & Gravatt,C.C. (1977): *CRC Crit. Rev. Anal. Chem.*, 6, 361
7) Cali,J.P. & Reed,W.P. (1976): *NBS Special Publication 422*, "Accuracy in Trace Analysis: Sampling, Sample Handling and Analysis", La Fleur,P.D. (ed), Vol. 1, p41-63
8) Paulsen,P.J. (1977): *NBS Special Publication 492*, "Procedures Used at the National Bureau of Standards to Determine Selected Trace Elements in Biological and Botanical Materials", Mavrodineanu R. (ed), p33-48
9) Cali,J.P., Mandel,J., Moore,L. & Young,D. S. (1972): *NBS Special Publication 260-36*, "A Referee Method for the Determination of Calcium in Serum", p63-81
10) Grubbs,F. E. & Beck,G. (1972): *Technometrics*, 14, 847
11) Pearson,E.S. & Stephens,M. A. (1964): *Biometrika*, 51, 484

Acknowledgements

We are indebted to the collaborating laboratories for their co-operation and particularly to members of the research group on CRMs under the chairmanship of Professor Toshiyasu Kiba (Kanazawa Institute of Technology). Without the endeavour of the participating laboratories the certified values for Pond Sediment could not have been issued. The assistance and co-operation afforded by the National Bureau of Standards, U.S.A. also is gratefully acknowledged. Special thanks are due to Dr. C.W. McLeod for correction of English and Mrs H. Sakaguchi who undertook offset typing of the original manuscripts.

環境標準試料「池底質」の調製，分析及び保証値

計測技術部　岡本研作（編）

近年の環境問題の深刻化に伴い，様々な環境試料の分析が行われている。環境試料は組成が複雑なこと，安定性及び均一性に乏しいこと，測定対象物質の濃度が低いことなどの理由により，その分析は一般的に難しく，分析値は信頼性に乏しいと考えられている。環境の評価や政策の決定は環境分析の結果に基づいて行われるので，環境試料の分析において最も重要なことは"正確な"分析値を得ることである。

分析値の正確さを向上し，確証するために，①正確さが証明された標準分析法を用いる方法，②構成各成分の化学分析値が確定された標準試料を用いる方法，が通常用いられる。実際の化学分析においては，各実験室の設備や装置，化学者の熟練度が異なるため，分析方法自身についての評価を行うことは時間や費用の制約もあってかなり難しく，現実には標準試料という物質を用いて測定システムの正確さを校正、評価することになる。このように，標準試料は化学分析において基準物質として使われ，そのうえにたって分析化学的方法が開発される学問上の重要な基礎となっている。社会的にも，品質保証，精度管理，環境分析などの基準として，標準試料の重要性は年々増大している。

標準試料は元来，商工業製品の品質の公正化，商取引の円滑化を図るために作製されたものである。現在でも標準試料の大部分は商工業に関連した金属，ガラスなどであり，生物や環境試料などの天然物を用いて調製した"Soft"な標準試料の歴史は比較的新しく，1970年代初めにＮＢＳ（National Bureau of Standards，米国標準局）から配布された Orchard Leaves（果樹葉），Bovine Liver（子牛肝臓）が代表的なものである。ＮＢＳから引き続き数種類の環境標準試料が配布されており，IAEA（International Atomic Energy Agency; 国際原子力機関）などの国際機関では近年標準試料のプログラムを強力に推進している。このように，標準試料は社会的要求を直接的に反映しており，近年の環境問題の広がりに伴い分析方法の開発や分析精度の管理向上のために，とくに天然物を用いてその化学組成が確定された標準試料の重要性が再認識されてきた。

以上のような背景をふまえ，計測技術部では，分析化学的な基礎研究に加えて，環境分析の精度向上に資するため，「環境標準試料の作製と評価に関する研究」を経常研究の一つとして昭和52年度より開始した。この中で最初に環境標準試料として作り上げた「リョウブ」（Pepperbush，NIES No.1）については，国立公害研究所研究報告，第18号「Preparation, Analysis and Certification of PEPPERBUSH Standard Reference Material」(1980)の中で，詳しく記載されている。本研究報告書は，リョウブに続いてNIES No.2として完成された環境標準試料「池底質」(Pond Sediment) について調製法，分析法および保証値を

中心として記載してあり，7章から成る。

国立公害研究所で現在使用できる分析方法は限られているので，標準試料の保証値を決定するためには，様々な分析技術をもつ研究機関と協同で分析することが不可欠である。国立公害研究所では，このような主旨から，分析化学に長年従事されている20名の方々に池底質試料の分析依頼を行い，分析結果を提供していただいた。第6章を執筆していただいた小山睦夫助教授（京都大学原子炉実験所）もその一人であり，特に中性子放射化分析法がこの研究に極めて重要であることから，理論と分析結果が第6章として記載されている。

第1章　環境分析における底質試料

Sediments in Environmental Analysis

計測技術部　岡本研作

本章は，この報告書における序として，環境分析の目的と現状，環境試料—特に底質試料の特徴，底質標準試料の現状および国立公害研究所における標準試料プログラムについて述べる。

環境分析の主たる目的は，現在の環境の質を正しく把握し，環境の変化を検知してその起源や機構を解明し，環境の保全に努めるとともに将来の変化に対処することにある。このために，おびただしい数の環境試料の分析が行われている。環境分析において現在もっとも要求されていることは，分析値の正確さである。たとえば過去の分析値が信頼性に乏しいため，測定対象物質の経時変化を追跡できないという問題が起こっているし，また正確な分析法が確立されていないために行政的対応が出来ない場合もある。

環境分析における分析値の正確さを向上させるためには，①正確さが証明された標準分析法を用いる方法，②構成各成分の化学分析値が確定された環境標準試料を用いる方法があり，両者は同時にまたは単独で用いられる。標準分析法としてはJIS や環境庁で定められた方法が用いられているが，いまだ十分とは言えない。ここでは，標準試料という"物質"を用いて分析値の正確さを評価し，向上させるという立場から，環境分析と標準試料について考える。

底質は，形成される時に有機物や無機物を取り込むので周囲の環境を直接的に反映していると言え，過去の気候や地質の変化および人間活動の記録となり，特に理想的な条件下では環境汚染の貴重な記録となる。実際に，湖底や海底から底質の"コアサンプル"を採取して，年代別に様々の角度から測定が行われている。また，底質は吸着，イオン交換などの化学反応や生物活動の結果として重金属を濃縮するので，水中の濃度が低すぎて測定できない場合にも，底質試料中の重金属は容易に測定することができるので，周囲の環境を知ることができる。特に人工的な有機化合物については，ある時期に突然発見され，しだいに増え続けるという現象が明瞭に現れる。有機物は底質中で重要な役割を果しており，例えば重金属と結

合してそれを不溶化または可溶化したり，時には揮散させることがある。

底質は極めて複雑な性質をもつので，底質試料の分析にあたっては細心の注意が必要である。試料は均一性に乏しいので良く混合することが必要であり，試料の乾燥条件，pH，Ehなどに注意する必要がある。底質試料の分析結果を表す場合，「全分解法」または「溶出法」のどちらに基づくかを決めなければならない。前者の場合には，アルカリ溶融法やフッ化水素酸を用いた酸分解法が地球化学や分析化学の分野で広く用いられている。「溶出法」の場合には，0.1規定塩酸やＥＤＴＡを用いた溶出法が土壌学や植物栄養学で用いられている。どちらの方法を採用するかは研究目的による訳で，標準試料の分野では「全分解法」に基づく保証値が定められている。池底質試料の分析結果も，「全分解法」に基づいて表されている。

地球化学の分野では，米国地質調査所を中心として様々な岩石標準試料が配布されている。これに対して，底質標準試料は，調製，分析ともに難しいことから，その数は限られている。環境庁では近年，「関東ローム」「河川底質」を共通試料として，Cd，Cr，As などの分析値のクロスチェックを行ったが，未だに分析値のばらつきが大きい。ＮＢＳからは「River Sediment」が配布されており，IAEAでは「Lake Sediment」について推薦値を定めている。他の関連機関でも底質標準試料を作製中であり，こうした中で国立公害研究所から「池底質」標準試料が配布されることの意義は大きい。

NIES №1「リョウブ」，№2「池底質」に続いて，№3「クロレラ」についても保証値が最近定められた。人体試料は環境試料の中でも特に重要なものであり，№4「人血清」，№5「頭髪」の分析が進行中である。生物を使った環境モニタリングの一つとして，ムラサキイガイ（Mussel）を使って海洋の汚染を監視することが世界的に広く行われている。NIES №6として「ムラサキイガイ」粉末の標準試料を調製し，現在，分析を進めている。「リョウブ」「池底質」に続いて，これらの試料についても，国立公害研究所報告としてまとめられる予定である。

第2章　池底質試料の調製

Preparation of Pond Sediment

計測技術部　岡本研作
東京大学理学部　岩田泰夫

国立公害研究所では，環境分析における底質試料の重要性を考慮して，NIES №2として底質標準試料の調製を行った。東京大学三四郎池の底質（約500kg）を採取し，２ｍｍのふるいを通して異物を除去した後，フィルター上に集めて約２週間風乾した。風乾試料はアルミナボールミル中で粉砕し，ナイロン製ふるい（50，100，200メッシュ）を通して最も均一

性が良かった200メッシュ以下の試料を標準試料の調製に使用した。約40kg（200メッシュ以下）の試料を2分器を11回通して均一化し，2,000本のガラスビンに約20gずつ充塡した。底質試料は微生物の作用を受けやすいため，殺菌操作を行うことが必要である。池底質試料では，コバルト－60照射による殺菌を行った。

標準試料として確立されるためには，まず試料の均一性が良いことが不可欠である。池底質試料の均一性を調べるために，11本の試料をランダムに選び，1ビンから3試料をとって酸分解―原子吸光法により重金属を定量し，ビン間のばらつきを推定した。同じ試料を国立公害研究所と東京大学で独立に分析した結果，試料間のばらつきは極めて小さく，標準試料として十分に均一なことが判明した。

底質のように有機物含量が高い試料については，試料の乾燥条件を注意深く選ぶ必要がある。熱天秤を用いた実験から110℃で4時間乾燥すれば恒量に達することが示され，また共同分析の結果，この条件で再現性の良い水分減量が得られたので，池底質標準試料の乾燥条件として110℃，4時間が設定されている。

第3章　X線光電子分光法による池底質の表面化学組成の分析

Analysis of the Surface Chemical Composition of Pond Sediment by X-ray Photoelectron Spectroscopy

計測技術部　瀬山春彦
〃　　相馬光之

池底質標準試料は非常に均一な粉末であるが，粉末を構成している各粒子別にみれば，当然，異なった化学組成を持った幾種類もの粒子の混合物である。更に個々の粒子も何種類かの化学物質の複合したものであると考えられ，粒子の表面の化学組成もまたバルクの組成とは異なっているであろう。特に底質粒子の表面の化学組成は粒子の起源に依存するばかりでなく，環境中で，物質の沈着や溶脱などによる変化をうけている可能性があり，いわば底質試料の来歴に依存しているものと考えられる。表面の化学組成に関する知見は，バルクの化学物質組成，粒度別元素組成などとともに，試料の特性を示すものとして，標準試料を使用するに際し，有用な知見となろう。X線光電子分光法（XPS）は，X線照射によって放出される電子のエネルギー分布を測定し，放出電子の属した元素を同定する分析法であるが，固体の表面数十Å程度の厚さの層の元素組成，元素の属する化学種に関する知見を，試料の非破壊的測定によって与える点でユニークな分析法である。

本章では，XPSの原理を簡単に紹介したあと，定量分析の手続を，底質試料分析の目的に即して概説し，C，N，O，Al，Ca，Fe，Mg，Na，P，Si，Ti などの主成分元素の表面層における平均組成の測定結果を述べ，更にスペクトル線の位置から得られる各元素の化

学結合状態についての知見を略述した。表面の元素組成を他章で詳述されているバルクの元素組成と比較すると，表面層では，有機物に帰属されるC，Nの濃度が高く，この有機物により部分的に"希釈"されている以外は変化の少ないSi，Tiなど，おそらく溶脱により表面層で著しく欠乏しているNaなど，吸着により表面濃縮の過程もあると考えられるFe，Pなどに区別できることが明らかとなった。

第4章　原子吸光法による池底質試料の分析

Analysis of Pond Sediment by Atomic Absorption Spectrometry

計測技術部　岡本研作

池底質試料の分解には，硝酸—フッ化水素酸—過塩素酸を使った酸分解法を用いた。通常，1g試料を酸分解して100mlとした試料を原子吸光分析に用いたが，DDTC—MIBK抽出法を用いてCdやPbなどの分析を行った。ヒ素の分析では，底質調査法の硝酸—硫酸分解法を用いた。

底質中のCaやMgの分析では，大量に存在するAlの妨害作用を除くため，Laを添加して標準添加法を行うことが望ましい。Zn，Cu，Pb，Ni，Coでは，検量線法，標準添加法，溶媒抽出法ともに，比較的一致した値を得た。Cdの原子吸光分析では，共存元素の影響を防ぐため，溶媒抽出することが必要である。Crの分析では，試料の前処理としてアルカリ溶融法が良く，酸分解法では低い分析値を与える。また，ヒ素の水素化物を発生させる操作では共存物質の影響を受けやすいので，標準添加法を用いる必要がある。水銀の分析では，加熱気化—銀トラップ原子吸光法とゼーマン水銀分析計を用い，一致した値を得た。

第5章　プラズマ発光分析法による池底質試料の分析

Analysis of Pond Sediment by Inductively Coupled Plasma Atomic Emission Spectrometry

計測技術部　岡本研作
〃　西川雅高
〃　C. W. McLeod

プラズマ発光分析法（ICP）は，高感度，化学干渉が少ないこと，検量線の直線範囲が広いこと，多元素同時分析などの優れた特長のゆえに，近年，急速に環境分析に用いられてきた。しかし，ICP分析法の一つの問題点は分光干渉であり，特に底質のようにFe，Alなどの主成分元素の存在下で微量元素の定量を行う場合には，細心の注意が必要である。分光干渉は，①発光線の重なり，②バックグランドのシフト，に分けられる。底質の分析では，ある

程度の分光干渉は装置的にやむを得ないので，問題はいかにしてこうした干渉作用を定量化して，測定値を正しく補正するかということになる。分光干渉を補正するために，①補正係数法，②マトリックスマッチ法，③溶媒抽出法を比較検討した。補正係数法は，直続式ポリクロメーター方式の分光器では実用的な方法であり，池底質試料についてもある程度保証値と一致した値を得た。しかし，この場合は，試料の液性に基づく物理干渉の影響を無視できず，試料はできる限り希釈して標準溶液と液性を合わせる方が良い。マトリックスマッチ法は，試料中と同じ濃度の主成分元素を標準溶液（Low，High共）に加えるので，分光干渉の問題が消去され，また物理干渉も液性を合わせたことにより無視できる。マトリックスマッチ法により保証値と良く一致した値を得たが，本法の問題点は組成が似た試料についてしか適用できないこと，試薬（主成分元素）中の不純物の影響を受けることである。溶媒抽出法は，分光干渉を示す主成分元素をあらかじめ除去するという意味で優れているが，同時に抽出できる元素は限られていること，操作が繁雑であることなどの欠点がある。

底質試料のICP分析における分光干渉の例として，Ti 228.618nm の発光線によるCo 228.616nm分析線へのスペクトル線干渉をとりあげ，SITを検出器とする分光器およびエシェル分光器による池底質溶液のTi，Coの発光スペクトルを示した。

第6章　中性子スペクトルモニターを用いる中性子放射化分析による「池底質」及び「岩石」標準試料の分析

Analysis of Pond Sediment and Rock Reference Materials by Instrumental Neutron Activation Analysis with the Use of Neutron Spectrum Monitors

水質土壌環境部　高松武次郎
滋賀大学教育学部　川嶋　宗継
京都大学原子炉実験所　松下　録治
〃　小山　睦夫

中性子放射化分析法は非破壊多元素同時分析法として広く環境試料に適用されて来た。これには二つの測定法がある。一方は"相対法"と呼ばれ，分析元素の標準と試料を同時に照射し，冷却時間を補正した両者のγ線ピーク強度の比較から元素濃度を求める方法である。この方法は分析元素種があまり多くない場合には有効である。他方は，"絶対法"あるいは"フラックスモニター法"と呼ばれる。この方法では，中性子束密度や種々の核定数（放射化断面積，天然存在比，γ線分岐比等），検出器の効率等の数値から，直接試料中の元素濃度が算出される。通常，少数のフラックスモニターを試料と同時に照射し，計算時に中性子（熱中性子と熱外中性子）束密度の変動を補正する。この方法は核定数等の数値に多少の不確定性

を含むが，多元素の同時分析に際し，面倒な標準の調製が不要である他，計算機処理にも適している点が優れている。

ここでは，フラックスモニター法で「池底質」標準試料と「岩石」標準試料（JG—1，地質調査所）を分析した。方法を次に示す。(1)長寿命核種の分析：約200 mg の試料をポリエチレン管に精秤，封入し，フラックスモニターとしてミリポアフィルターに添着したCo（50μg），Cr（50μg），Sb（20μg）及びU（11.3 μg）と共に京都大学原子炉（KUR）の圧気輸送管（№2）で1時間照射した。試料は8～10日冷却後，53ccのGe（Li）検出器を備えた4Kチャンネルパルスハイトアナライザーでγ線スペクトルを測定して，結果を磁気テープに収録した。元素濃度はプログラム"COVIDN"や"GAMMA"により，ミニコンピューターで算出した。(2)短寿命核種の分析：試料の20～30mgをポリエチレン管に封入し，Mn（100 μg）と共に5分間照射した。約2時間冷却後，(1)と同様に分析した。以上の方法により標準試料中の23元素を定量した。結果にはけい光X線分析で求めた8元素の分析値も合わせて示した。

第7章　池底質試料の保証値

The Certification of Pond Sediment

計測技術部　岡本研作

標準試料は，標準となるべき化学分析値が確定されて初めて実用に供される。標準試料の保証値（または標準値）を決定するためには，その元素に対してできる限り多くの原理が異なった分析方法が用いられ，しかも分析値が一致することが必須となる。国立公害研究所で現在使用できる分析方法は限られているので，様々な分析技術をもつ研究機関と共同で池底質試料の分析を行った。池底質試料の分析には，①原子吸光法，②炎光光度法，③プラズマ発光分析法，④けい光X線分析法，⑤同位体希釈質量分析法，⑥中性子放射化分析法，⑦光量子放射化分析法，⑧吸光光度法，⑨けい光光度法，⑩重量分析法，⑪容量分析法，⑫ポテンシオメトリーが用いられた。

国立公害研究所では，保証値を決定した元素は，原則として，(1)絶対分析法による二つ以上の独立した分析値があること，または，(2)二つ以上の独立した比較分析法による分析値があることを基準としている。しかし，(1)の絶対分析法のみによって保証値を決めることは現状では不可能であるので，(2)の様式を用いてこれに絶対分析法による分析値も含めることになる。池底質試料の場合には，保証値を決定した各元素に対して，3種類以上の原理が異なった分析方法が用いられた。

鉛を例として，保証値を決定した方法を示す。鉛の保証値（105 μg/g）は，同位体希釈質量分析法（絶対分析法）による分析値及び異常値を棄却した後の11個の分析値（原子吸光法，

プラズマ発光分析法，光量子放射化分析法による）の平均値であり，その不確定性（±6μg）は11個の分析値の標準偏差の2倍及び各分析方法の平均値の95%信頼区間を含む範囲として定められている。

池底質試料中の13元素（Al, Fe, Ca, K, Na, Zn, Cu, Pb, Cr, Ni, Co, As, Cd）について保証値が，12元素（Si, Ti, P, Mn, V, Sr, Rb, Sc, La, Br, Sb, Hg）について参考値が定められている。

謝　辞

標準試料の保証値を決めるためには，様々な分析技術をもつ研究機関と共同で分析を行うことが不可欠であり，池底質試料の分析にあたっては多くの方々の御協力をいただいた。特に，文部省科研費環境科学特別研究研究班「環境分析データ記載法の標準化の研究」（班長木羽敏泰金沢工大教授）の皆様からは，様々な分析方法による貴重な分析値を提供していただき，分析値を本報告書に収録することに格別の御配慮をいただいた。このような御協力があったからこそ，池底質試料の保証値を決定することが可能になったと考える。また，小山助教授には本報告書のために執筆の労をとっていただいた。御協力をいただいた皆様に厚く感謝いたします。

研究報告既刊リスト

国立公害研究所特別研究成果報告

第 1 号　陸水域の富栄養化に関する総合研究 ── 霞ケ浦を対象域として ── 昭和51年度．（1977）

第 2 号　陸上植物による大気汚染環境の評価と改善に関する基礎的研究 ── 昭和51／52年度研究報告．（1978）

（改　称）

国立公害研究所研究報告

第 3 号　A comparative study of adults and immature stages of nine Japanese species of the genus *Chironomus* (Diptera, Chironomidae). (1978)
（日本産ユスリカ科 Chironomus 属 9 種の成虫，サナギ，幼虫の形態の比較）

第 4 号　スモッグチャンバーによる炭化水素 ─ 窒素酸化物系光化学反応の研究 ── 昭和52年度中間報告．（1978）

第 5 号　芳香族炭化水素 ─ 窒素酸化物系の光酸化反応機構と光酸化二次生成物の培養細胞に及ぼす影響に関する研究 ── 昭和51／52年度研究報告．（1978）

第 6 号　陸水域の富栄養化に関する総合研究（Ⅱ）── 霞ケ浦を中心として ── 昭和53年度．（1979）

第 7 号　A morphological study of adults and immature stages of 20 Japanese species of the family Chironomidae (Diptera). (1979)
（日本産ユスリカ科20種の成虫，サナギ，幼虫の形態学的研究）

第 8 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 ── 昭和52／53年度研究報告．（1979）

第 9 号　スモッグチャンバーによる炭化水素 ─ 窒素酸化物系光化学反応の研究 ── 昭和53年度中間報告．（1979）

第 10 号　陸上植物による大気汚染環境の評価と改善に関する基礎的研究 ── 昭和51／53年度特別研究報告．（1979）

第 11 号　Studies on the effects of air pollutants on plants and mechanisms of phytotoxicity. (1980)
（大気汚染物質の植物影響およびその植物毒性の機構に関する研究）

第 12 号　Multielement analysis studies by flame and inductively coupled plasma spectroscopy utilizing computer-controlled instrumentation. (1980)
（コンピュータ制御装置を利用したフレームおよび誘導結合プラズマ分析法による多元素同時分析）

第 13 号　Studies on chironomid midges of the Tama River. (1980)
Part 1. The distribution of chironomid species in a tributary in relation to the degree of pollution with sewage water.
Part 2. Description of 20 species of Chironominae recovered from a tributary.
（多摩川に発生するユスリカの研究
── 第 1 報　その一支流に見出されたユスリカ各種の分布と下水による汚染度との関係 ──
── 第 2 報　その一支流に見出された Chironominae 亜科の20種について ──）

第 14 号　有機廃棄物，合成有機化合物，重金属等の土壌生態系に及ぼす影響と浄化に関する研究 ── 昭和53，54年度特別研究報告．（1980）

第 15 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 ── 昭和54年度特別研究報告．（1980）

第 16 号　計測車レーザーレーダーによる大気汚染遠隔計測．（1980）

第 17 号　流体の運動および輸送過程に及ぼす浮力効果 ── 臨海地域の気象特性と大気拡散現象の研究 ── 和和53／54年度特別研究報告．（1980）

第 18 号　Preparation, analysis and certification of PEPPERBUSH standard reference material.（1980）
（環境標準試料「リョウブ」の調製，分析および保証値）

第 19 号　陸水域の富栄養化に関する総合研究（Ⅲ）── 霞ケ浦（西浦）の湖流 ── 昭和53／54年度．（1981）

第 20 号　陸水域の富栄養化に関する総合研究（Ⅳ）── 霞ケ流流域の地形，気象水文特性およびその湖水環境に及ぼす影響 ── 昭和53／54年度．（1981）

第 21 号　陸水域の富栄養化に関する総合研究（Ⅴ）── 霞ケ浦流入河川の流出負荷量とその評価 ── 昭和53／54年度．（1981）

第 22 号　陸水域の富栄養化に関する総合研究（Ⅵ）── 霞ケ浦の生態系の構造と生物現存量 ── 昭和53／54年度．（1981）

第 23 号　陸水域の富栄養化に関する総合研究（Ⅶ）── 湖沼の富栄養化状態指標に関する基礎的研究 ── 昭和53／54年度．（1981）

第 24 号　陸水域の富栄養化に関する総合研究（Ⅷ）── 富栄養化が湖利用に及ぼす影響の定量化に関する研究 ── 昭和53／54年度．（1981）

第 25 号　陸水域の富栄養化に関する総合研究（Ⅸ）── Microcystis（藍藻類）の増殖特性 ── 昭和53／54年度．（1981）

第 26 号　陸水域の富栄養化に関する総合研究（Ⅹ）── 藻類培養試験法によるＡＧＰの測定 ── 昭和53／54年度．（1981）

第 27 号　陸水域の富栄養化に関する総合研究（Ⅺ）── 研究総括 ── 昭和53／54年度．（1981）

第 28 号　複合大気汚染の植物影響に関する研究 ── 昭和54／55年度特別研究報告．（1981）

第 29 号　Studies on chironomid midges of the Tama River.（1981）
Part 3. Species of the subfamily Orthocladiinae recorded at the summer survey and their distribution in relation to the pollution with sewage waters.
Part 4. Chironomidae recorded at a winter survey.
（多摩川に発生するユスリカ類の研究
── 第３報　夏期の調査で見出されたエリユスリカ亜科 Orthocladiinae 各種の記載と，その分布の下水汚染度との関係について ──
── 第４報　南浅川の冬期の調査で見出された各種の分布と記載 ──）

第 30 号　海域における富栄養化と赤潮の発生機構に関する基礎的研究 ── 昭和54／55年度特別研究報告．（1982）

第 31 号　大気汚染物質の単一および複合汚染の生体に対する影響に関する実験的研究 ── 昭和55年度特別研究報告．（1981）

第 32 号　スモックチャンバーによる炭化水素 ─ 窒素酸化物系光化学反応の研究 ── 昭和54年度特別研究中間報告 ── 環境大気中における光化学二次汚染物質生成機構の研究（フィールド研究１）．（1982）

第 33 号　臨海地域の気象特性と大気拡散現象の研究 ── 大気運動と大気拡散過程のシミュレーション ── 昭和55年度特別研究報告．（1982）

第 34 号　環境汚染の遠隔計測・評価手法の開発に関する研究 ── 昭和55年度特別研究報告．（1982）

第 35 号　環境面よりみた地域交通体系の評価に関する総合解析研究．（1982）

第 36 号　環境試料による汚染の長期モニタリング手法に関する研究 ── 昭和55，56年度特別研究報告．（1982）

第 37 号　環境施策のシステム分析支援技術の開発に関する研究（1982）

第 38 号　Preparation, analysis and certification of POND SEDIMENT certified reference material. (1982)
（環境標準試料「地底質」の調製，分析および保証値）

Report of Special Research the National Institute for Environmental Studies

No. 1* Man activity and aquatic environment—with special references to Lake Kasumegaura —Progress report in 1966. (1977)

No. 2* Studies on evaluation and amelioration of air pollution by plants—Progress report in 1976-1977. (1978)

[Starting with Report No. 3, the new title for NIES Report was changed to :]

Research Report from the National Institute for Environmental Studies

No. 3 A comparative study of adults and immature stages of nine Japanese species of the genus *Chironomus* (Diptera, Chironomidae). (1978)

No. 4* Smog chamber studies on photochemical reactions of hydrocarvon-nitrogen oxides system —Progress report in 1977. (1978)

No. 5* Studies on the photooxidation products of the alkylbenzene-nitrogen oxides system, and on their effects on Cultured Cells—Research report in 1976-1977. (1978)

No. 6* Man activity and aquatic environment—with special references to Lake Kasumigaura —Progress report in 1977-1978. (1979)

No. 7 A morphological study of adults and immature stages of 20 Japanese species of the family Chironomidae (Diptera). (1979)

No. 8* Studies on the biological effects of single and combined exposure of air pollutants—Research report in 1977-1978. (1979)

No. 9* Smog chamber studies on photochemical reactions of hydrocarvon-nitrogen oxides system —Progress report in 1978. (1979)

No. 10* Studies on evaluation and amelioration of air pollution by plans—Progress report in 1976-1978. (1979)

No. 11 Studies on the effects of air pollutants on plants and mechamisms of phytotoxicity. (1980)

No. 12 Multielement analysis studies by flame and inductively coupled plasma spectroscopy utilizing computer-controlled instrumentation. (1980)

No. 13 Studies on chironomid midges of the Tama River. (1980)

Part 1. The distribution of chironomid species in a tributary in relation to the degree of pollution with sewage water.

Part 2. Description of 20 species of Chironominae recovered from a tributary.

No. 14* Studies on the effect of organic wastes on the soil ecosystem—Progress report in 1978-1979. (1980)

No. 15* Studies on the biological effects of single and combined exposure of air pollutants—Research report in 1979. (1980)

No. 16* Remote measurement of air pollution by a mobile laser radar. (1980)

No. 17* Influence of buoyancy on fluid motions and transport processes—Meteorological characteristics and atmospheric diffusion phenomena in the coastal region—Progress report in 1978-1979. (1980)

No. 18 Preparation, analysis and certification of PEPPERBUSH standard reference material. (1980)

No. 19* Comprehensive studies on the eutrophication of fresh-water areas—Lake current of Kasumigaura (Nishiura)—1978-1979. (1981)

No. 20* Comprehensive studies on the eutrophication of fresh-water areas—Geomorphological and hydrometeorological characteristics of Kasumigaura watershed as related to the lake environment—1978-1979. (1981)

No. 21* Comprehensive studies on the eutrophication of fresh-water areas—Variation of pollutant load by influent rivers to Lake Kasumigaura—1978-1979. (1981)

No. 22* Comprehensive studies on the eutrophication of fresh-water areas—Structure of ecosystem and standing crops in Lake Kasumigaura—1978-1979. (1981)

No. 23* Comprehensive studies on the eutrophication of fresh-water areas—Applicability of trophic state indices for lakes—1978-1979. (1981)

No. 24* Comprehensive studies on the eutrophication of fresh-water areas—Quantitative analysis of eutrophication effects on man's utilization of lake water resources—1978-1979. (1981)

No. 25* Comprehensive studies on the eutrophication of fresh-water areas—Growth characteristics of blue-green-algae, *microcystis*—1981-1979. (1981)

No. 26* Comprehensive studies on the eutrophication of fresh-water areas—Determination of argal growth potential by algal assay procedure—1978-1979. (1981)

No. 27* Comprehensive studies on the eutrophication of fresh-water areas—Summary of Researches —1978-1979. (1981)

No. 28* Studies on effects of air pollutant mixtures on plants—Progress report in 1979-1980. (1981)

No. 29 Studies on chironomid midges of the Tama River. (1981)

Part 3. Species of the subfamily Orthocladiinae recorded at the summer survey and their distribution in relation to the pollution with sewage waters.

Part 4. Chironomidae recorded at a winter survey.

No. 30* Eutrophication and red tides in the coastal marine environment—Progress report in 1979-1980. (1982)

No. 31* Studies on the biological effects of single and combined exposure of air pollutants—Research report in 1980. (1981)

No. 32* Smog chamber studies on photochemical reactions of hydrocarbon-nitrogen oxides system —Progress report in 1979—Research on the photochemical secondary pollutants formation mechanism in the environmental atmosphere (Part 1). (1982)

No. 33* Meteorological characteristics and atmospheric diffusion phenomena in the coastal region —Simulation of atmospheric motions and diffusion processes—Progress report in 1980. (1982)

No. 34* The development and evaluation of remote measurement methods for environmental pollution—Research report in 1980. (1982)

No. 35* Comprehensive evaluation of environmental impacts of road and traffic. (1982)

No. 36* Studies on the method for long term environmental monitoring—Progress report in 1980-1981. (1982)

No. 37* Study on supporting technology for systems analysis of environmental policy. (1982)

No. 38 Preparation, analysis and certification of POND SEDIMENT certified reference material. (1982)

* in Japanese