

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON MICROCHEMICAL TECHNIQUES AND
TRACE ANALYSIS*

Separation and Preconcentration of Trace Substances – V

MICROSCALE PRECONCENTRATION TECHNIQUES FOR TRACE ANALYSIS

Prepared for publication by

G. TÖLG¹, A. MIZUIKE², YU. A. ZOLOTOV³, M. HIRAIDE² and
N. M. KUZ'MIN³

¹Institute of Spectrochemistry & Applied Spectroscopy, Bunsen-Kirchhoff-Str. 11, D-4600 Dortmund 1, FRG

²Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

³Vernadskii Institute of Geochemistry & Analytical Chemistry, Kosygin Str. 19, Moscow V-334, USSR

*Membership of the Commission during the period (1983–1987) this report was prepared was as follows:

Chairman: B. Griepink (Netherlands); *Secretary:* A. Townshend (UK: 1983–85); D. E. Wells (UK: 1985–87); *Titular Members:* K. Biemann (USA); E. Jackwerth (FRG); A. Lamotte (France); Z. Marczenko (Poland); Yu. A. Zolotov (USSR); *Associate Members:* K. Ballschmiter (FRG); K. Beyermann (FRG: 1983–85); R. Dams (Belgium); K. Fuwa (Japan); M. Grasserbauer (Austria); W. Gries (FRG); K. Heinrich (USA: 1983–85); M. W. Linscheid (FRG: 1985–87); A. Mizuike (Japan: 1983–85); H. Muntau (Italy: 1985–87); J. M. Ottaway (UK: 1983–85); M. J. Pellin (USA: 1985–87); B. Ya. Spivakov (USSR: 1985–87); G. Tölg (FRG: 1983–85); A. Townshend (UK: 1985–87); D. E. Wells (UK: 1983–85); D. G. Westmoreland (USA: 1985–87); *National Representatives:* R. Gijbels (Belgium); H. Thoma (Brazil: 1983–85); Z.-M. Ni (Chinese Chemical Society: 1985–87); J. Janak (Czechoslovakia: 1983–85); M. J.-F. Leroy (France); Z. Horvath (Hungary: 1983–85); M. Sankar Das (India: 1983–85); S. M. Khopkar (India: 1985–87); R. C. H. Hsia (Malaysia: 1983–85); A. D. Campbell (New Zealand); B. Salbu (Norway: 1983–85); W. Kemula (Poland: 1983–85); A. Cedergren (Sweden); J. M. Ottaway (UK: 1985–87); E. A. Terent'eva (USSR).

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1988 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Separation and Preconcentration of Trace Substances – V. Microscale preconcentration techniques for trace analysis

Abstract-The determination of elemental traces in micro samples, i.e., micro-trace analysis can be successfully carried out by combining preconcentration steps with modern instrumental determination methods. In this paper, the problems and their solutions for each analytical stage of micro-trace analysis are presented and briefly discussed. Some typical examples of micro-trace analysis are also reviewed.

INTRODUCTION

Micro-trace analysis is the determination of elemental traces at ng - pg levels by using small amounts of sample (<100 mg). Micro-trace analysis is necessary or desirable in the following cases.

- (1) When sample amounts are limited. For example, some kinds of samples are expensive, toxic, rare and available only in small amounts or form toxic or strongly active compounds during the sample treatment.
- (2) When the distribution of elemental traces or sample inhomogeneity is studied.
- (3) When microscale analytical procedures are assumed to be superior to conventional ones. For example, high-purity reagents and expensive materials are economized and the sample decomposition and preconcentration are more rapid and easier.

Methods for micro-trace analysis can be divided into the following two groups:

- (1) direct instrumental methods in which the sample is directly excited to produce a signal proportional to the concentration of elemental traces, and
- (2) combined procedures including sample decomposition and preconcentration of elemental traces, frequently in combination with instrumental determination methods.

Although most modern instrumental determination methods offer excellent absolute detection limits (ref. 1), combined procedures consisting of several stages, i.e., sampling and sample preparation, weighing, decomposition, preconcentration and determination allow a substantial improvement in the relative detection limits as well as of the precision and accuracy of the analytical results (Table 1). There are also other advantages of such combinations.

In the present paper the individual stages of typical procedures are discussed and evaluated.

PROBLEMS OF MICRO-TRACE ANALYSIS AND THEIR SOLUTION BY COMBINED PROCEDURES

General remarks

With decreasing sample size, the following problems arise or become more serious: inhomogeneity of the sample, change of the property of the sample, increase of evaporation and adsorption, difficulty in handling small amounts of materials, etc. Accordingly, to obtain reliable analytical results in micro-trace analysis, special apparatus and procedures must be developed. For a minimization of contamination and losses of elemental traces, one should decrease the number of analytical steps (e.g., decomposition combined with simultaneous preconcentration), select suitable materials for vessels (e.g., quartz or PTFE), use a single vessel throughout the whole procedure, and carry out the analysis in a clean room or a closed system.

TABLE 1. Evaluation of methods for micro-trace analysis

Items	Direct instrumental methods	Combined procedures (combination of different methods)
Interferences	Strong interelement and matrix interferences may occur.	Interferences can be eliminated by separating elemental traces from the matrix and other co-existing elements.
Detectability	Detection limits depend on the signal generation area and the sensitivity of the detector.	Elemental traces in the sample are totally concentrated into a small volume, which strongly increases the concentrations of the elements.
Calibration	Reference materials are required.	Calibration may be done easily with the aid of standard solutions.
Systematic errors	Contamination and losses are minimized; blank problems are minimized.	Contamination, adsorption and volatilization hazards are increased and the errors of the individual steps accumulate. However, these problems can be overcome by careful operations.
Economical aspects	Simultaneous multielement determinations are easy and rapid (computer-assisted evaluation).	Labor, time and skill are generally required, but by using well-designed apparatus and techniques the methods can also be carried out easily and rapidly.
Micro-distribution analysis	Most suitable	Possible

Sampling and sample preparation

A knowledge of the origin and history of the sample is necessary for simplifying the analytical procedure and minimizing errors. The manner of sample preparation is determined by its physical and chemical properties. Stable, non-volatile, non-hygroscopic and soluble samples can be handled most easily. It must be kept in mind, however, that the properties of the sample may be changed by reducing the sample amount; this may lead to an increase of volatility and instability because of high surface-to-volume ratio, change of element valency and other modifications.

When working on the microscale, it must be taken into account that elemental traces may be inhomogeneously distributed in the solid sample. Homogenization of samples may be achieved by grinding, crushing and mixing. Small and closed vibrating pulverizers made of agate, corundum, tungsten carbide, boron carbide, etc. should be used in order to minimize contamination during grinding. Contamination due to airborne dust can be avoided by using clean hoods or benches with a laminar-airflow.

Weighing

In the development of balances, efforts have been made to allow accurate work with smaller samples. At present, weighing errors are negligible compared to those due to other sources. Two types of balances (ref. 2) have been widely accepted, namely the quartz fiber torsion balances (readability 0.005 μg , capacity 0.2 g) and electromagnetic balances (readability 0.05 - 0.1 μg , capacity 2 g).

Weighing and decomposition should be performed in the same vessel preferably of platinum, quartz or high-purity aluminium.

Decomposition

Several decomposition methods established in conventional trace analysis (refs. 3, 4) can also be applied to micro-trace procedures. However, the increase in the ratio of the surface area to sample volume may enhance evaporation, adsorption or desorption. Furthermore, spluttering of very tiny particles of sample may lead to serious errors. Therefore, the decomposition methods and vessels used (dimension, shape, construction material, etc.) should be carefully selected and optimized. Vessels made of quartz, PTFE, glassy carbon, polypropylene and platinum are suitable. Decomposition in a high pressure PTFE bomb or low-temperature combustion with activated oxygen is sometimes useful. The decomposition of micro-samples is well-treated in ref. 2.

The reagents used should be selected with the following points in mind: effective decomposition, purity or ease of purification, simple removal after decomposition and stability during storage. Many useful purification techniques have been reported (refs. 2, 5 - 7).

The decomposition leads to a substantial preconcentration when elemental traces are released as gaseous or volatile compounds (oxides, halides, hydrides, etc.). This effect may simplify the analytical procedure substantially and increase the accuracy of the analytical results (refs. 2,5).

Preconcentration

When using specially designed apparatus and techniques instead of simply scaling-down macro-facilities, microscale preconcentration may become easy and rapid without causing a deterioration in the analytical precision and accuracy. Moreover, well-designed microscale preconcentration offers the following advantages over conventional operations.

- (1) High-purity reagents are used in such small amounts that the analyst can prepare them himself, e.g., in the case of ultrahigh-purity liquids by isothermal distillation or sub-boiling distillation.
- (2) Sample decomposition and preconcentration are more rapid and easier.
- (3) The sample treatment and preconcentration can be achieved in the determination system itself (e.g., in a graphite electrode in the case of optical emission spectrometry).
- (4) The quantity of waste is minimized.
- (5) The working bench area is reduced.

The most important preconcentration techniques are volatilization, electrodeposition, liquid-liquid extraction, coprecipitation and ion exchange.

1. Volatilization. Although a close coupling of the decomposition and preconcentration steps is desirable, it cannot always be realized in practice. Frequently, elemental traces are separated by volatilization after sample decomposition. The transfer of volatile products to absorption vessels may present difficulties, which can be overcome in most cases by using non-reactive carrier gases or water vapour. The volatile compounds are then absorbed in a small volume of a suitable solution.

The Kjeldahl method used in micro-trace analysis (Fig. 1, ref. 8) differs from the conventional one in the following points:

- (1) The sample is decomposed in a high pressure PTFE bomb instead of the usual decomposition in an open system, in order to minimize contamination.
- (2) Water vapour for transferring the ammonia to the absorption vessel is generated in the vessel itself so as to keep the distillate at a constant volume, this being as small as possible.
- (3) The ammonia is immediately titrated in the absorption vessel with a coulometrically generated titrant and electrochemical determination of the end point.

2. Electrodeposition. Electrodeposition of noble metals, mercury, cobalt, copper, zinc, lead, etc., is very convenient as the contamination hazard due to reagents is very small. An almost quantitative deposition on a small electrode surface can be achieved by circulating the sample solution over or through the cathode (Fig. 2, ref. 9).

When in anodic stripping voltammetry the electrolyte volume is reduced from conventional milliliter to microliter levels, a shorter pre-electrolysis time suffices for the deposition (refs. 10 - 12).

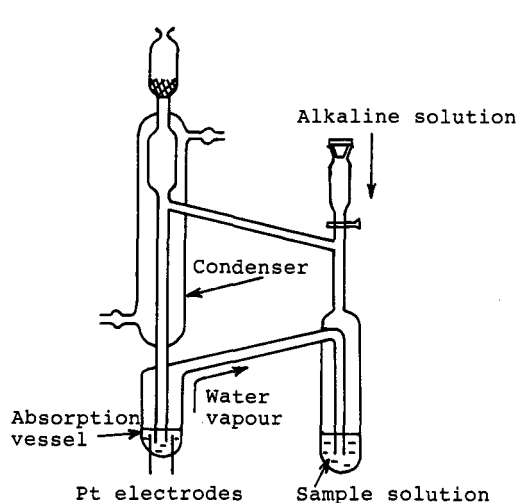


Fig. 1. Volatilization

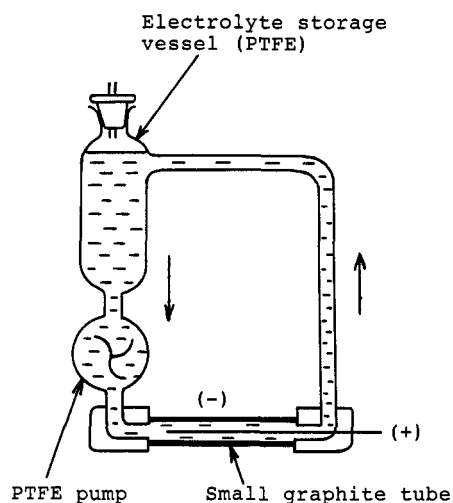


Fig. 2. Electrodeposition

3. Liquid-liquid extraction. In micro-trace analysis, conventional separatory funnels are not suitable, because their volumes are too large and the solution is lost by distribution in and around the stopcock. A small test tube with a PTFE or polyethylene stopper is convenient. A conical centrifuge tube with a stopper is also useful. Extraction may be carried out by manual shaking, but a more effective mixing can be achieved by using a mechanical rotary vibrator. After standing or centrifuging, the phases are separated from each other with the aid of a suitable suction device such as a small pipette or piston syringe.

4. Coprecipitation. The reliable isolation of the precipitates containing elemental traces may be obtained by centrifugation. In many cases, glass centrifuge tubes can be substituted advantageously by plastic ones. After centrifugation, the supernatant solution is removed by suction or decantation. Precipitates having densities near unity are successfully isolated by filtration with small membrane filters.

5. Ion exchange. Capillary columns packed with small amounts of ion exchange resins or thin precipitate layers (ref. 13) which trap elemental traces by ion exchange may be used. Columns can be made of quartz, polyethylene or PTFE. Papers impregnated with finely ground ion exchange resins are also useful.

Determination

After concentration and separation, the elemental traces may be determined with sufficient precision and accuracy by optical emission spectrometry, atomic absorption and fluorescence spectrometry, mass spectrometry, gas chromatography, flow-injection analysis, electron, ion and laser microprobe methods, etc. In many cases, maximum sample volumes are in the microliter range. Microtitration is also useful, provided enough sample is available. The selection of the determination method depends upon its sensitivity and selectivity, the number of elemental traces to be determined (simultaneous multielement determination or single-element determination) and compatibility with the preceding decomposition and preconcentration steps.

EXAMPLES

To illustrate the ideas and principles of combined procedures in micro-trace analysis, some selected examples are presented in Table 2.

CONCLUSION

Properly designed preconcentration techniques operated in the microliter range may be used effectively in inorganic trace analysis in order to minimize sample size, volumes of high-purity reagents required, wastes produced, and analysis time. Further improvements in apparatus and procedures, in automation and in the development of new application fields are expected in the future.

TABLE 2. Applications of microscale preconcentration techniques (selection)

Samples	Elemental traces	Preconcentration techniques	Determination methods	References
<u>Industrial</u>				
Iron, copper, molybdenum, lead (<100 mg)	S ($\mu\text{g/g}$)	Volatilization as hydrogen sulphide	Microtitration	14
Aluminium, zirconium, niobium (<100 mg)	B ($\mu\text{g/g}$ -ng/g)	Volatilization as fluoride	MIP-OES	15
Manganese, iron, copper, molybdenum, silver, tungsten, etc. (<100 mg)	Impurities	Fractional volatilization	OES	16
Iron, copper, niobium, molybdenum, tantalum (<100 mg)	Si, As ($\mu\text{g/g}$)	Volatilization by chlorination	MS, ICP-OES	17,18
Zinc (0.5-1 mg)	Pb (low $\mu\text{g/g}$)	Electrodeposition on silver-plated glassy carbon electrode	ASV	10
Nickel (0.5-1 mg)	Cu, Pb (low $\mu\text{g/g}$ -ng/g)	Electrodeposition on silver-plated glassy carbon electrode	ASV	11
Tantalum (10 mg)	Cu (ng/g)	Adsorption on a cation exchange column	OES	19
Lead (2-5 mg)	Ag (low $\mu\text{g/g}$ -ng/g)	Adsorption on suspended dithizone powder	Furnace AAS	20
Cadmium (<50 mg)	Cu ($\mu\text{g/g}$)	Selective dissolution of metal phthalocyanines with sulphuric acid	AAS	21
Silicon (10 mg)	Al, Ag, Au, Bi, etc. ($\mu\text{g/g}$ -ng/g)	Volatilization of silicon as fluoride	OES	22
Silicon, germanium, III-V compounds (10-50 mg)	Cu, Cd, Sn, Sb, Te, Pb, Bi ($\mu\text{g/g}$)	Electrodeposition	ASV	23,24
Gallium arsenide (5 mg)	Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, In, Sn, Pb, Bi ($\mu\text{g/g}$ -ng/g)	Adsorption of gallium on PTFE checkerwork by extraction chromatography after volatilization of arsenic	OES	25
Titanium dioxide (1-10 mg)	Pb (low $\mu\text{g/g}$ -ng/g)	Electrodeposition on glassy carbon electrode	ASV	12
Titanium dioxide (5-10 mg)	V (low $\mu\text{g/g}$)	Extraction with sodium diethyldithiocarbamate and chloroform	Furnace AAS	26
Petroleum pitch (10 mg)	Al, Fe (low $\mu\text{g/g}$)	Volatilization of matrix by plasma ashing	Furnace AAS	27

TABLE 2 (continued)

Samples	Elemental traces	Preconcentration techniques	Determination methods	References
<u>Geological</u>				
Lunar igneous rocks (<100 mg)	N ($\mu\text{g/g}$)	Volatilization as ammonia	Coulometric titration	8
<u>Biological</u>				
Flour, liver, hair (<100 mg)	Se (low $\mu\text{g/g}$ - ng/g)	Volatilization as oxide	AAS	28
Flour, leaf, liver, hair, nail (0.3 - 10 mg)	Se (ng/g - pg/g)	Volatilization as hydride followed by adsorption on silanized Chromosorb W	Furnace AAS	29
Hair (<100 mg), blood (1 ml)	Be (ng/g)	Extraction with tri-fluoroacetylacetone and benzene	Chelate-GC	30
Blood, serum (1 ml)	Be (ng/g)	Extraction with acetylacetone and benzene	Furnace AAS	31
Urine (1 ml)	Be (low ng/g)	Extraction with acetylacetone and benzene	Furnace AAS	32
Brain tissue (1 - 10 mg)	Zn ($\mu\text{g/g}$)	Adsorption on an anion exchange column	Isotope dilution-MS	33
<u>Environmental</u>				
Sediment, soil (<100 mg)	Hg (ng/g)	Decomposition in a microwave induced oxygen plasma	MIP-OES	34
Seawater (0.5 ml)	Cd (pg/g)	Adsorption on a single anion exchange bead	Furnace AAS	35
Polluted seawater (1 - 2 ml)	Cu, Zn, Cd, Pb ($\mu\text{g/g}$)	Adsorption on a chelating resin column	AAS (flow injection)	36
Rain water (2 ml)	V (low ng/g - pg/g)	Adsorption on an anion exchange column	Catalytic spectrophotometry (flow injection)	37
Suspended solids in fresh waters (0.2 - 3 mg)	Cr, Cu, Cd ($\mu\text{g/g}$)	Selective dissolution with 1 M ammonium acetate followed by 0.1 M hydrochloric acid	Furnace AAS	38
Humic substances in fresh waters (0.1 mg)	Cu, Cd, Pb ($\mu\text{g/g}$)	Selective dissolution with 4 M nitric acid and a macroreticular anion exchanger	Furnace AAS	39

MIP: Microwave induced plasma, OES: Optical emission spectrometry, MS: Mass spectrometry, ICP: Inductively coupled plasma, ASV: Anodic stripping voltammetry, AAS: Atomic absorption spectrometry, GC: Gas chromatography.

REFERENCES

1. J. A. C. Broekaert, Optical Emission Spectral Analysis with High-Frequency and Microwave Induced Plasma Sources (Habilitation at the University of Antwerp) Wilrijk (1985).
2. G. Tölg, Elemental Analysis with Minute Samples, in Comprehensive Analytical Chemistry III, G. Svehla, ed., Elsevier, Amsterdam (1975).
3. P. Tschöpel, Aufschlussmethoden, in Ullmanns Encyklopädie der technischen Chemie 5, p. 27, Verlag Chemie, Weinheim (1980).
4. G. Knapp, Fresenius' Z. Anal. Chem. 317, 213 (1984).
5. P. Tschöpel and G. Tölg, J. Trace and Microprobe Techniques 1, 1 (1982).
6. A. Mizuike, Enrichment Techniques for Inorganic Trace Analysis, p. 17, Springer, Berlin (1983).
7. M. Zief and J. W. Mitchell, Contamination Control in Trace Element Analysis, p. 98, Wiley, New York (1976).
8. O. Müller, E. Grallath and G. Tölg, Proc. Lunar Sci. Conf. 7th., 1615 (1976).
9. G. Volland, P. Tschöpel and G. Tölg, Anal. Chim. Acta 90, 15 (1977).
10. T. Miwa, Y. Nishimura and A. Mizuike, Anal. Chim. Acta 140, 59 (1982).
11. T. Miwa, S. Rubi and A. Mizuike, Bunseki Kagaku 32, E49 (1983).
12. L. Jin, J. Xu, T. Miwa and A. Mizuike, Mikrochim. Acta [Wien] 1983III, 245 (1983).
13. A. Disam, P. Tschöpel and G. Tölg, Fresenius' Z. Anal. Chem. 295, 97 (1979).
14. A. Watson, E. Grallath, G. Kaiser and G. Tölg, Anal. Chim. Acta 100, 413 (1978).
15. E. Grallath, P. Tschöpel, G. Kölblin, U. Stix and G. Tölg, Fresenius' Z. Anal. Chem. 302, 40 (1980).
16. Kh. I. Zilbershtein, ed., Spektral'nyi analiz chistykh veshchestv (spectrochemical analysis of pure substances) Leningrad, Khimiya Publ. House, 1971.
17. L. B. Kuznetsov, V. N. Belyaev and G. G. Kovalev, Zh. Anal. Khim. 38, 1800 (1983).
18. L. B. Kuznetsov, V. N. Belyaev and V. P. Baluda, Zh. Anal. Khim. 39, 215 (1984).
19. E. Kitazume, T. Sakamoto, H. Kawaguchi and A. Mizuike, Bunseki Kagaku 27, 566 (1978).
20. A. Mizuike, M. Hiraide and S. Kawakubo, Mikrochim. Acta [Wien] 1979II, 487 (1979).
21. S. Kawakubo, T. Fukasawa, T. Chino and A. Mizuike, Bunseki Kagaku 32, 395 (1983).
22. I. A. Kuzovlev, V. L. Sabatovskaya, O. A. Sverdlina, L. S. Khorkina, M. S. Vinogradova and N. M. Kuz'min, Zavodsk. Lab. 37, 1071 (1971).
23. Problemy analiticheskoi khimii, T. IV. Sovremennye metody analiza mikroob'ektov i tonkikh plenok (Problems of analytical chemistry, Volume IV. Modern methods of analysis of microsamples and thin films) Moscow, Nauka Publ. House (1977).
24. I. R. Shelpakova, I. G. Yudelevich and B. M. Ayupov, Posloinyi analiz materialov elektronnoi tekhniki (Layer-by-layer analysis of materials of electronics) Novosibirsk, Nauka Publ. House (1984).
25. N. M. Kuz'min, A. V. Emel'yanov, S. V. Meshchankina, V. L. Sabatovskaya, I. A. Kuzovlev and T. I. Zakharova, Zh. Anal. Khim. 26, 282 (1971).
26. S. Kawakubo, S. Yamaguchi and A. Mizuike, Bunseki Kagaku 30, 594 (1981).
27. T. Miwa, T. Maiya and A. Mizuike, Bunseki Kagaku 32, 393 (1983).
28. A. Meyer, Ch. Hofer, G. Knapp and G. Tölg, Fresenius' Z. Anal. Chem. 305, 1 (1981).
29. J. Piwonka, G. Kaiser and G. Tölg, Fresenius' Z. Anal. Chem. 321, 225 (1985).
30. G. Kaiser, E. Grallath, P. Tschöpel and G. Tölg, Fresenius' Z. Anal. Chem. 259, 257 (1972).
31. T. Stiefel, K. Schulze, G. Tölg and H. Zorn, Fresenius' Z. Anal. Chem. 300, 189 (1980).
32. T. Stiefel, K. Schulze, G. Tölg and H. Zorn, Anal. Chim. Acta 87, 67 (1976).
33. M. A. Klitenick, C. J. Frederickson and W. I. Manton, Anal. Chem. 55, 921 (1983).
34. G. Kaiser, D. Götz, G. Tölg, G. Knapp, B. Maichin and H. Spitzky, Fresenius' Z. Anal. Chem. 291, 278 (1978).
35. M. Koide, D. S. Lee and M. O. Stallard, Anal. Chem. 56, 1956 (1984).
36. S. Olsen, L. C. R. Pessenda, J. Ruzicka and B. H. Hansen, Analyst 108, 905 (1983).
37. T. Fukasawa, S. Kawakubo, T. Okabe and A. Mizuike, Bunseki Kagaku 33, 609 (1984).
38. S. P. Tillekeratne, M. Hiraide and A. Mizuike, Mikrochim. Acta [Wien] 1984III, 69 (1984).
39. M. Hiraide, S. P. Tillekeratne, A. Otsuka and A. Mizuike, Anal. Chim. Acta 172, 215 (1985).