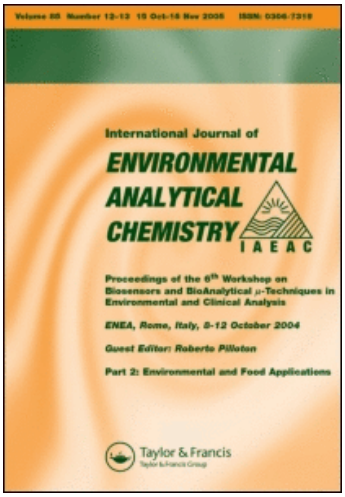

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Atomic Absorption Spectrometric and Spectrophotometric Trace Analysis of Germanium in Environmental Samples with N-p-Bromophenyl-2-Furylacrylohydroxamic Acid and Phenylfluorone

S. A. Abbasi[abc]
[a] Water Quality and Environment Division, Centre for Water Resources Development and Management, Kozhikode, India [b] Adjunct Professor, Sonoma State University, California, USA [c] Professor, School of Ecology, Pondicherry Central University, Pondicherry

To cite this Article Abbasi, S. A.(1988) 'Atomic Absorption Spectrometric and Spectrophotometric Trace Analysis of Germanium in Environmental Samples with N-p-Bromophenyl-2-Furylacrylohydroxamic Acid and Phenylfluorone', International Journal of Environmental Analytical Chemistry, 33: 2, 149 — 160
To link to this Article: DOI: 10.1080/03067318808081233
URL: http://dx.doi.org/10.1080/03067318808081233

Intern. J. Environ. Anal. Chem., Vol. 33, pp. 149–160
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Great Britain

Atomic Absorption Spectrometric and Spectrophotometric Trace Analysis of Germanium in Environmental Samples with N-p-Bromophenyl-2-Furylacrylohydroxamic Acid and Phenylfluorone

S. A. ABBASI*†

Water Quality and Environment Division, Centre for Water Resources Development and Management, Kozhikode 673 571, India

(*Received 17 June 1987; in final form 22 November 1987*)

N-Phenyl-2-furylacrylohydroxamic acid and its nine analogues in conjunction with eight different chromogening agents were explored for the selective extraction and sensitive determination of germanium (IV). The combination of N-p-bromophenyl-2-furylacrylohydroxamic acid (BFHA) and phenylfluorone was found to be the most sensitive and selective. Germanium was extracted with BFHA into chloroform and phenylfluorone was added to the extract. The resulting ternary germanium-BFHA-phenylfluorone complex was measured spectrophotometrically at its absorption maxima of 500 nm ($\varepsilon = 1.3 \times 10^5\,mol^{-1}\,cm^{-1}$). For the atomic absorption spectrometric (AAS) determination, germanium was extracted with BFHA into methyl

*Concurrently: Adjunct Professor, Sonoma State University, California 949228, USA.

†Present address: Professor, School of Ecology, Pondicherry Central University, Pondicherry 605 001.

isobutyl ketone and measured directly at 265.1 nm using nitrous oxide-acetylene flame. Both the instrumental methods were successfully applied to the determination of germanium in soils, biological materials, and natural waters.

KEY WORDS: Germanium, environment, analysis, atomic absorption spectrometry, spectrophotometry.

INTRODUCTION

Germanium is relatively abundant in the lithosphere; its average concentration has been estimated at 7 ppm.[1] Eruptive rocks contain on an average 1.5 ppm and metamorphic and sedimentary rocks 2 ppm of germanium.[2,3] Iron meteorites have been found to contain 0.3–500 ppm, tektites 0.04–0.6 ppm and lunar materials 0.001–1.8 ppm of germanium.[4] Analytical data on the concentration of germanium in soils is scarce and the available information has largely been generated through spectrographic methods whose sensitivity for the given metal has been questioned.[5] In general, germanium levels in soils have been found to be low—less than 3 ppm— the highest concentrations (14–17 ppm) have been determined in Madagascar in ferrallitic soils formed on granite or cipolin.

The abundance of germanium and its proximity with the biologically active trace elements (atomic numbers 25–30, 33–35) has evoked interest in the biological role of this metal. Schroeder and Balassa[6] examined 125 samples of foods and beverages and detected germanium in all of them. Four of these samples contained more than 2 ppm and 15 others more than 1 ppm of germanium. The metal was not detected in refined wheat flour, although it was present in whole wheat and was concentrated in barn. The mean levels in groups of vegetables and leguminous seeds were 0.15 and 0.45 ppm respectively (fresh weight basis). Similar concentrations were observed in meat and in dairy products.

Information on the germanium content of normal animal organs is scarce while no report is available on human organs in particular. The liver, kidneys, heart, lungs and spleen of laboratory mice and rats fed normal diets were shown[7] to contain germanium in concentrations ranging from 0.10 to 2.79 ppm (wet weight). When mice were given 5 ppm germanium in the drinking water for their

lifetime, higher concentrations were found in these organs, especially in the spleen, but rat tissues accumulated very little germanium under these conditions.[7,8] The germanium in the drinking water at this level gave evidence of toxicity in both species in terms of reduced life span and increased incidence of fatty degeneration of the liver.

Little is known of the metabolism of the germanium ingested from ordinary diets.[9] Rosenfeld[10] found that oral doses of sodium germanate were rapidly and almost completely absorbed from the gastro intestinal tract within a few hours and were excreted largely in the urine during 4 to 7 days. These findings are substantiated by Schroeder and Balassa[5] who found that dietary germanium is well absorbed and excreted largely via the kidneys in man. These authors calculated that adults ingest approximately 1.5 mg Ge in the daily diet of which 93% appears in the urine and the rest in the faeces.

Germanium is widely used in industry as a semiconductor especially in transistors but, unlike silicon, tin, and lead, which precede or follow germanium in the group IVb of the periodic table, there are no reports on the concentration of germanium in the mining or industrial waste emissions. One of the main reasons of the paucity of information on the environmental status of germanium appears to be the lack of rapid analytical methods of appropriate sensitivity and selectivity.[2,11–13] The best detection limit is 50 ppm with flame AAS and 0.5 ppm with inductively coupled plasma spectroscopy and electrothermal AAS.[11–14] Even the microwave and capacitively coupled high-frequency plasma source spectroscopy, which enables the analysis of several metals at sub-ppm levels, can achieve a detection limit of only 1.5 ppm in case of germanium.[12,13] The selectivity is also low and it is not possible to employ these methods to the determination of germanium in environmental matrices.[13] In this paper we report methods for the atomic absorption spectrometric (AAS) and spectrophotometric determination of submicrogram levels of germanium in environmental samples on the basis of chelation and selective extraction with a new reagent N-*p*-bromophenyl-2-furylacrylohydroxamic acid (BFHA). In the AAS method the germanium-BFHA chelate is extracted into methyl isobutyl ketone (MIBK) and determined with nitrous oxide-acetylene flame at the 265.1 nm resonance line. The spectrophotometric method is based on the

extraction of germanium from 7 M HCl medium with BFHA in chloroform. Phenylfluorone is added to the extract to form an intensely coloured Ge (IV)-BFHA-phenylfluorone ternary complex which is measured at 500 nm ($\varepsilon = 1.3 \times 10^5$ l mole^{-1} cm^{-1}). BFHA was selected from a series of hydroxamic acid derivatives (Table 1) as it was found to have maximum selectivity and sensitivity for germanium. We have earlier employed hydroxamic acid derivatives of furan-2-carboxylic acid for the trace analysis of titanium,[15] vanadium[16] and cerium.[17] We subsequently prepared hydroxamic acid derivatives of furan-2-acrylic acid and as expected the increased conjugation in the acrylo derivatives resulted in significant enhancement relative to the acids derived from furan-2-carboxylic acids.

EXPERIMENTAL

Reagents and apparatus

All chemicals were of guaranteed reagent or equivalent grade unless otherwise specified. Water was deionised and doubly distilled.

Hydroxamic acids were synthesised by coupling the *para* or *meta* substituted phenylhydroxylamines with the oxychloride of furan-2-acrylic acid by the general method of Tandon and Bhattacharyya.[18] The acids were repeatedly crystallised from benzene to constant, sharp, melting points and were characterised by IR and UV spectroscopy, as detailed elsewhere.[19] Solutions of hydroxamic acids (0.01 M) were made in chloroform (for spectrophotometric studies) and in MIBK (for AAS studies). The phenylfluorone solution was prepared by dissolving 0.1 g of the reagent in a solvent mixture containing 100 ml methanol and 0.5 ml HCl. For preparing the standard germanium solution, 0.104 g of germanium dioxide was added to 45 ml water containing 1.5 g sodium hydroxide and the mixture was boiled to dissolve the solids. The solution was cooled and made upto 100 ml in a calibrated volumetric flask.

The pH adjustments were done with Radiometer model PHM 29 and Industrial Electronics Corporation model 092 pH meters after precalibration with standard buffers of pH 4 and 9. The spectrophotometric measurements were carried out on Perkin–Elmer model

402 and Hitachi model 220 spectrophotometers using matched quartz cells. For atomic absorption spectrometric studies Techtron model AA-3 and Instrumentation Laboratory model IL 951 instruments, equipped with hallow cathode lamps for germanium (265.1 nm line) were used.

Analytical procedure

(*a*) *For spectrophotometric analysis:* A sample solution of the metal was made 7 M in HCl by adding appropriate volume of concentrated HCl and was transferred to a 100 ml separatory funnel. To it 10 ml of 0.01 M hydroxamic acid in chloroform was added and the contents were shaken vigorously for 5 minutes. The phases were allowed to separate and the organic layer was drained in a beaker containing anhydrous sodium sulphate to free it from entrapped water and was collected in a 25 ml calibrated flask. The extraction was repeated with 2–3 ml reagent solution and was added to the previous extract. To ensure complete recovery of germanium the sodium sulphate was washed with 2–3 ml of chloroform and the washings added to the previously collected extracts. Finally 1 ml of 0.1 % solution of phenylfluorone and 4 ml of methanol were added to the extracts and the contents were diluted to 25 ml with chloroform. The absorbance was measured at 500 nm against the reagent blank prepared in the same way but in absence of germanium.

(*b*) *For atomic absorption spectrometric analysis:* For atomic absorption spectrometric analysis, germanium (IV) was extracted with a 0.01 M hydroxamic acid solution in MIBK. The optimum extraction time was 10+3 minutes. In other respects the extraction procedure was exactly the same as the one described above for the spectrophotometric studies, except that MIBK was used in place of chloroform and there was no addition of phenylfluorone-methanol solution. For AAS measurements the MIBK extract was aspirated into nitrous oxide–acetylene flame. The hollow cathode lamp providing 265.1 nm line at lamp current of 14 mA was used. The light beam was 10 nm above the burner head and the flow rates of nitrous oxide and acetylene were set at 3.2 l min^{-1} and 4.5 l min^{-1} respectively. MIBK blank was used as reference.

RESULTS AND DISCUSSION

Choice of hydroxamic acid and the extracting solvents

The spectrophotometric characteristics of germanium-hydroxamic-acid-phenylfluorone ternary systems are presented in Table 1. BFHA is seen to give the most sensitive colour reaction. Similar trends in sensitivity were observed when benzene, carbon tetrachloride and MIBK were used as extracting solvents in place of chloroform but the spectrophotometric sensitivity was always the highest with chloroform as illustrated with germanium-BFHA-phenylfluorone system in Table 2. Therefore chloroform was chosen as solvent for spectrophotometric analysis. However, MIBK was preferred for AAS analysis because MIBK extracts gave a little higher absorbance than chloroform or carbon tetrachloride extracts of similar germanium (IV) levels. Also, the chlorinated solvents tended to produce pungent gases in flame and were a potential hazard to the analyst. This drawback of the chlorinated solvents, and the suitability of MIBK as carrier solvent in the AAS analysis, has been reported.[20,21]

Table 1 Spectral characteristics of ternary systems involving germanium(IV), hydroxamic acids and phenylfluorone

Hydroxamic acid	*Wavelength of maximum absorbance of the ternary system*[a] λ_{max}, *nm*	*Molar absorptivity at* λ_{max}, $l\ mol^{-1}\ cm^{-1}$
N-*p*-Methoxyphenyl-2-furylacrylo-	498	9.8×10^4
N-*m*-Methoxyphenyl-2-furylacrylo-	495	9.2×10^4
N-*p*-Tolyl-2-furylacrylo-	495	9.0×10^4
N-*m*-Tolyl-2-furylacrylo-	492	8.8×10^4
N-Phenyl-2-furylacrylo-	490	8.7×10^4
N-*p*-Chlorophenyl-2-furylacrylo-	498	1.0×10^5
N-*p*-Bromophenyl-2-furylacrylo-	500	1.3×10^5
N-*m*-Bromophenyl-2-furylacrylo-	500	1.1×10^5
N-*p*-Iodophenyl-2-furylacrylo-	495	1.0×10^5
N-*p*-Nitrophenyl-2-furylacrylo-	485	7.5×10^4

[a]The reagents have negligible absorbance at these wavelengths.

Table 2 Spectral characteristics of germanium(IV)–BFHA–phenylfluorone system in different solvents

Solvent	*Wavelength of maximum absorbance, λ_{max}, nm*	*Molar absorptivity at λ_{max}, $l\,mol^{-1}\,cm^{-1}$*
Benzene	485	3.4×10^4
Methyl isobutyl ketone	488	7.3×10^4
Carbon tetrachloride	495	9.7×10^4
Chloroform	500	1.3×10^5

Optimisation of conditions for the extraction

With both chloroform and MIBK, the percentage extraction increased with the acidity of the medium. Complete extraction within 5 minutes of equilibration occurred from media 5.5–9 M in HCl (Figure 1). Longer durations for complete extraction were needed from $HClO_4$, HNO_3 or H_2SO_4 media and these acids also adversely affected the stability of the colour of the extract. All extractions were therefore done from 7 M HCl media.

The 0.01 M hydroxamic acid solutions in chloroform or MIBK were optimum for extraction; lower reagent concentrations prolonged the time of equilibration needed for complete germanium recovery while higher reagent concentrations had no significant improvement on the extraction time, though they did not have any adverse effect either.

Selection of phenylfluorone and optimisation of the phenylfluorone concentration

The germanium-hydroxamic acid extracts are colourless. They were usable directly in the AAS analysis but the addition of phenylfluorone was necessary to obtain a colour suitable for spectrophotometric measurements. The germanium-hydroxamic acid complexes had absorption peaks in the UV region at the wave-lengths (300–350 nm) at which the reagent blank also absorbed strongly, precluding the possibility of using those wavelengths for dependable

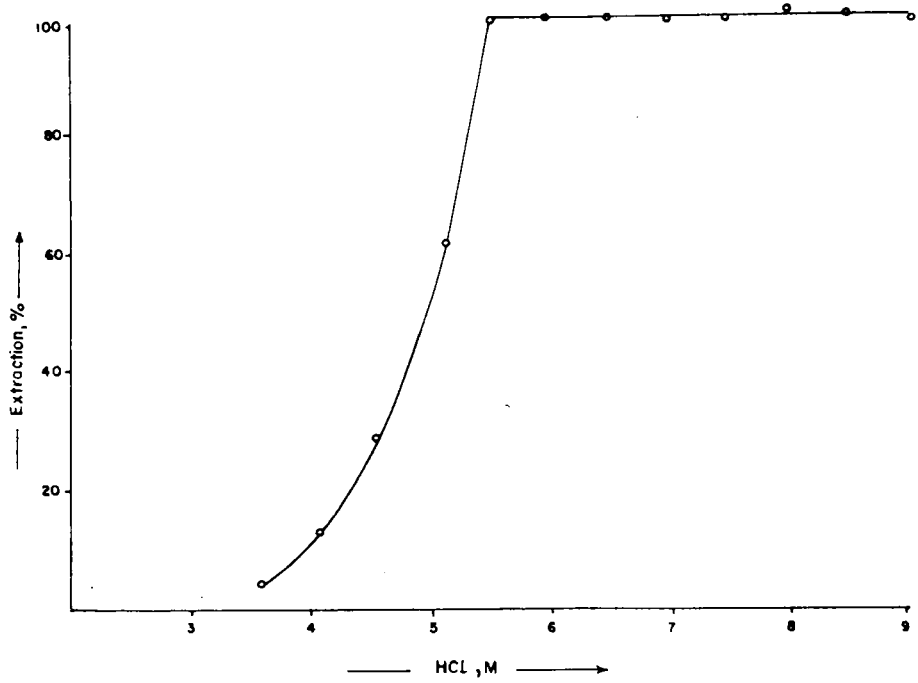

Figure 1 Extraction of germanium with BFHA in chloroform/MIBK as a function of HCl concentration.

analysis. We studied several ligands likely to form ternary complexes with germanium-BHFA systems and cause bathochromic shifts in the absorption maxima. The ligands included 1(2-pyridylazo)-2-naphthol (PAN), 4-(2-pyridylazo) resorcinol (PAR), 5-bromo-PAN, 5-bromo-PAR, 5-methyl-PAN, 5-methyl-PAR, 8-hydroxyquinoline and phenylfluorone. Of these only phenylfluorone caused the desirable bathochromic shift and by far the highest molar absorptivity. Various amounts of phenylfluorone solution in methanol were added to the germanium-BFHA extracts and it was found that 1 ml of 0.1 phenylfluorone was optimum for complete colour formation within 5 minutes of addition. The colour was stable for over 12 hours if protected from direct sunlight.

Enrichment potential

Germanium (5 μg) was extracted from 10 to 150 ml solutions into a set volume—10 ml—of organic phase and was determined spectrophotometrically. It was found that a change in the ratio of volumes of aqueous to organic phase from 1 to 10 does not adversely effect the germanium recovery within the equilibration time of 5+2 minutes. In other words the extraction system has the potential of enriching the sample up to 10 times, thus enhancing the effective sensitivity of the method of germanium 10-fold. Similar results were achieved with MIBK extraction and AAS determination.

Optical properties, calibration curves and sensitivity

(*a*) *Spectrophotometric analysis:* The red orange germanium-BFHA-phenylfluorone system obeys Beer's Law in the concentration range 0.01–0.65 ppm (mg l^{-1}) of germanium (IV) at 500 nm. The molar absorptivity and Sandell sensitivity[22] of the system are 1.3×10^5 l mol^{-1} cm^{-1} and 0.001 ppm respectively. The sensitivity can be enhanced 10-fold through enrichment, and by using quartz cells of 10 cm path length germanium levels as low as 10^{-4} ppm (0.1 ppb or 0.1 ng l^{-1}) can be determined.

(*b*) *Atomic absorption spectrometric analysis:* The concentration-absorbance curve was linear for 0.12–9 ppm of germanium at 265.1 nm line. The sensitivity for 1% absorption was 0.1 ppm. The sensitivity could be enhanced to 0.01 ppm through enrichment by solvent extraction.

Effect of diverse ions

The tolerance limits of the present method for various anions and cations in the spectrophotometric determination of 10 μg/25 ml (0.4 ppm) of germanium (IV) are presented in Table 3. A large number of anions and cations are tolerated when present in concentrations upto 50,000 times greater than germanium. Several other anions and cations commonly occurring in environmental matrices are also tolerated to a high degree. Such a level of selectivity is not possible if germanium is determined directly with

Table 3 Limits of tolerance of the present method towards foreign ions in the determination of 10 μg/25 ml of germanium(IV)

Foreign ion	*Tolerance limit, μg*
Li (I), Na (I), K (I), Rb (I), Cs (I), Be (II), Mg (II), Ca (III) Ba (II), Sr (II), Cu (II), Ni (II), Co (II), Mn (II), Zn (II), Cd (II), Hg (II), UO_2 (II), fluoride, chloride, bromide, sulphate, acetate, ascorbate, phosphate, acetate, nitrate, tartarate	> 500 000
Al (III), Ga (III), Pd (II), Ce (IV), Mo (VI), Ti (IV)[c], V (V)[a], Tl (III), La (IV), Th (IV), Bi (III), thiocyanate, borate	500 000
In (III), Cr (VI)[b], Nb[b]	300 000

[a]In presence of ascorbic acid as masking agent.
[b]In presence of tartaric acid as masking agent.
[c]In presence of fluoride as masking agent.

phenylfluorone;[13] prior extraction with BFHA either eliminates the potential interfering ions or reduces their concentrations below the tolerance limits. The tolerance limits for AAS determination were similar to these detailed in Table 3; prior extraction with BFHA-MIBK eliminated most of the matrix interferences.

DETERMINATION OF GERMANIUM IN SOILS, PLANT TISSUES ANIMAL TISSUES AND NATURAL WATERS

The soil samples were brought into solution by alkali fusion.[23] The plant tissue samples were washed with 50 g l^{-1} EDTA solution and then with de-ionised water.[24] This procedure was necessary to remove particulate matter adhering to the plant tissue surface. The animal tissue samples were washed thoroughly with physiological saline solution before final washing with water to remove any residual blood.[25]

The further processing of tissue samples involved[22–23] drying at 120 °C to a constant weight (referred as dry weight) and homogenising. Weighed quantities (100 mg) were heated with concentrated sulfuric acid (5 ml) on a hot plate at 70 °C for 5 minutes and nitric acid was added dropwise till all visible reaction ceased. The temper-

ature was raised to 100 °C and the heating was continued for 15 minutes. The reactants were taken off the hot plate, about 25 ml of water was added and the resultant solutions were cooled. If the solutions were cloudy, a few drops of hydrogen peroxide were added and gentle heat was applied till the digests were clear. They were finally made up to fixed volumes with water in calibrated flasks.

The water samples were filtered on site through 0.45 μm membrane filters and acidified to pH $\sim$ 1.8 with nitric acid as per standard methods.[26]

The results from spectrophotometric analysis are summarised in Table 4. To make sure that matrix is not influencing the analysis, germanium was determined with and without standard addition. The reliability of the method is reflected in the results. Replicate analysis of soil, plant tissue and spiked pond water samples (Table 4) by AAS yielded the values 1.08 ± 0.002, 1.41 ± 0.03 and 1.49 ± 0.004 which were in excellent agreement with the results obtained spectrophotometrically and with the probable true values.

Table 4 Analysis of germanium in soils, plant tissues, animal tissues and natural waters

Sample	*Germanium added*	*Germanium found (average of six) determinations)*	*Standard deviation*
Soil (brown sandy loam)	nil	1.09 ppm	0.04
	2.00 ppm	3.10 ppm	0.05
Seeds of black gram *Cicer aeretimium*	nil	1.39 ppm[a]	0.04
	2.00 ppm	3.41 ppm[a]	0.06
Muscle of frog *Rana tigrina*	nil	0.13 ppm[a]	0.003
	1.00 ppm	1.14 ppm[a]	0.007
	2.00 ppm	2.13 ppm[a]	0.03
River water	nil	nil	—
	1.00 ppm	0.98 ppm	0.006
	2.50 ppm	2.48 ppm	0.05
Pond water	nil	nil	—
	1.50 ppm	1.52 ppm	0.009

[a]In tissues dried at 120 °C

Acknowledgements

Thanks are due to the authorities of IIT Bombay, BITS Pilani, and CWRDM for providing facilities; to Mr. P. P. Venkitachalam of M/s Techno Instruments for the author to do AAS analysis; and to Ms. B. Kanchana for secretarial assistance.

References

1. H. Aubert and M. Pinta, *Trace Elements in Soils* (Elsevier, 1977), p. 109.
2. E. I. Hamilton. In: *Applied Soil Trace Elements*. B. E. Davies (ed.), (John Wiley, 1980), Ch. 3.
3. A. P. Vinogradov, *The Geochemistry of Rare and Dispersed Chemical Elements in Soils* (Consultants Bureau, New York, 1959), pp. 209.
4. H. Higuchi and J. W. Morgan, *Proc. Sixth Lun. Sci. Conf.* **2,** 1625 (1975).
5. L. Nalovic, *Cah. Orstom Sec. Pedol.* **7,** 133 (1969).
6. C. L. Lake and M. D. Campbell, *Anal. Chem.* **28,** 1273 (1956).
7. H. A. Shroeder and T. T. Balassa, *J. Nutr.* **92,** 245 (1967).
8. H. A. Shroeder, M. Kaniswa, D. V. Frost and M. Mitchener, *J. Nutr.* **96,** 37 (1968).
9. E. J. Underwood, *Trace Elements in Human and Animal Nutrition* (3rd Ed) (Academic Press, New York, 1971), p. 436.
10. G. Rosenfeld, *Arch. Biochem. Biophys.* **48,** 54 (1954).
11. M. Slavin, *Atomic Absorption Spectroscopy* (John Wiley, 1978), Ch. 6.
12. M. L. Parsons, S. Major and A. R. Forster, *Appl. Spectrosc.* **37,** 411 (1983).
13. V. J. Bhatt, Ph.D. Thesis, M.S. University of Baroda, 1985.
14. V. J. Koshy and V. N. Garg, *J. Scient. Industr. Res.* **45,** 294 (1986).
15. S. A. Abbasi, *Int. J. Env. Anal. Chem.* **11,** 1 (1982).
16. S. A. Abbasi, *Sep. Sc. Tech.* **15,** 1679 (1980).
17. S. A. Abbasi, *Sep. Sc. Tech.* **15,** 1789 (1980).
18. A. K. Majumdar, *N-Benzoylphenylhydroxylamine and its Analogues* (Pergamon, 1972), Ch. 3.
19. S. A. Abbasi, *Polish J. Chem.*, in press.
20. J. W. Robinson, P. F. Lott and A. J. Bernard, Jr. In: *Chelates in Analytical Chemistry* (H. A. Flaschka and A. J. Bernard, Jr., eds.), Vol. 4 (Marcel Dekker, New York, 1972), p. 233.
21. M. L. Harley, *Atomic Spectroscopy* **3,** 76 (1982).
22. E. B. Sandell, *Colorimetric Determination of Traces of Metals* (3rd Ed.) (Interscience, New York, 1959), p. 159.
23. S. L. Chopra and J. S. Kanwar, *Analytical Agricultural Chemistry* (Kalyani, New Delhi), 1976.
24. M. Pinta, *Detection and Determination of Trace Elements* (Ann Arbor Science, Michigan, 1973).
25. K. M. Samuel, *Clinical Laboratory Techniques* (Hoe & Co., Madras, 1977).
26. M. C. Rand, A. E. Greenberg and M. J. Tras, (Eds.), *Standard Methods for the Examination of Water and Wastewater* (14th Ed) (American Public Health Association, 1976), p. 145.