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SELECTIVE DETERMINATION OF ARSENITE BY FLOW INJECTION SPECTROPHOTOMETRY

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Summary—This paper describes the application of the well-known Molybdenum Blue method for selective determination of arsenite in a flow injection system. Selectivity is achieved by on-line separation of the main interferents phosphate, arsenate and silicate using a strong anion-exchange microcolumn located in the aspiration line of injection valve. Arsenite passing through the microcolumn unretained is determined using Molybdenum Blue method following in-line oxidation to arsenate by permanganate. A thorough investigation of optimal experimental conditions for both, the separation of interferents and sensitive detection of arsenite is presented. The method developed permits arsenite to be determined in the concentration range 5–500 μg/l with high precision and reliability. A sample throughput of 20 hr^{-1} is achieved. Phosphate, arsenate and silicate do not interfere at concentration levels significantly higher than that of arsenite. The application to real water samples reveals excellent recovery of spiked samples and the absence of matrix interferences.

Arsenic is an ubiquitous trace element which due to its toxicity has to be determined in a variety of environmental samples. Water is one of the important media through which humans are exposed to arsenic. In the absence of antropogenic sources well-waters may contain total arsenic concentrations as high as 100 μg/l. and considerably higher values can be found in polluted waters.[1] Permissable levels in drinking water are generally in the lower μg/l. range.

Arsenite and arsenate are the most common arsenic compounds in natural waters. Arsenoorganics, *e.g.* alkylarsenic acid and arsonium compounds, may also occur but their concentrations are generally extremely low. Because arsenic (III) is more toxic than arsenic (V) compounds[2,3] the concentration of arsenite in water samples is an important parameter for evaluation of water quality.

A variety of analytical methods exist to detect arsenic in environmental samples.[4] Atomic spectrometric methods following hydride formation[5–7] are by far the most popular methods but require comparatively expensive equipment and skillful operators. Moreover, the suitability of these methods to distinguish between the two oxidation states of arsenic is limited. Other methods like stripping voltammetry, neutron activation analysis and X-ray fluorescence are not useful for routine purposes in a large number of samples. Spectrophotometric methods for the determination of arsenic are unfashionable and are generally regarded to be insufficiently sensitive and selective. In order to overcome these limitations some means of preconcentration and matrix removal are commonly employed[8,9] which in turn prevent ready applicability in routine analysis.

A common spectrophotometric method for the determination of arsenate is based on formation of molybdoarsenic acid with subsequent reduction to Arsenomolybdenum Blue.[10] Since only arsenic (V) undergoes this reaction the method can be used for speciation purposes, arsenic (III) being determined after oxidative sample pretreatment and differencing the results. A serious limitation of the applicability of this method, in particular for environmental samples, is the interference of phosphate and silicate both of which form Molybdenum Blue. Silicate interference can be circumvented to a great extent by appropriate choice of reaction conditions, *i.e.* increasing acidity of the assay, masking and kinetic discrimination,[11] whereas

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phosphate reacts in the same way as arsenate with molar absorptivities of the two heteropoly blues being much the same.[12,13]

In order to apply the method for the determination of arsenate its separation from complex and potentially interfering matrices has been carried out.[14,15] However, the multistage procedures generally involved in the separation are time-consuming, carry a high risk of contamination and loss of analyte and are difficult to automize.

Flow injection analysis (FIA)[16,17] has proved to be a suitable technique for automation of wet chemical analytical methods. The controllable and reproducible conditions under which mixing of solutions, chemical reactions and separation steps take place result in unrivalled precision in particular when highly complex procedures are involved.[18,19]

FIA with spectrophotometric detection for the determination of arsenic has been the subject of two papers only.[20,21] Linares *et al.*[20] developed a method where phosphate, arsenate and arsenite are sequentially determined by formation of Molybdenum Blue. Chemical conditions are adjusted by means of switching valves to permit discrimination between individual species. Multiple calibrations are required and the concentrations of the arsenic species are calculated by differencing the results. Narusawa[21] used column separation of phosphate, arsenate and silicate in a flow injection system followed by on-line detection of Molybdenum Blue. This method is not suitable for the determination of arsenite.

In the present paper we suggest a method for selective and sensitive determination of arsenite. After removal of the interfering anions phosphate, arsenate and silicate by ion exchange, arsenite is oxidized to the pentavalent state which is then determined by the Molybdenum Blue method. The use of flow injection methodology is shown to allow all steps to be performed reliably on-line with high precision and sample throughput.

EXPERIMENTAL

Apparatus

The flow injection system comprised a multichannel peristaltic pump (Ismatec IPS-8, Zurich), an all-PTFE rotary injection valve with variable volume (Besta, Heidelberg) and a spectrophotometric detector (Model 5023, Tecator, Höganäs) equiped with an 18 μl volume, 10 mm path-length flow-through cuvette. A wavelength of 690 nm was set throughout. The detector was interfaced to a strip-chart recorder (Linseis, Selb). All flow lines and reaction coils were made from PTFE tubing of 0.5 mm i.d.

Ion exchange microcolumns were made from perspex tubes of 10 cm length and 3 mm i.d. The two ends of the tubes were machined to accept common chromatographic male nuts. In order to retain the column material nylon nets were inserted in the outlet.

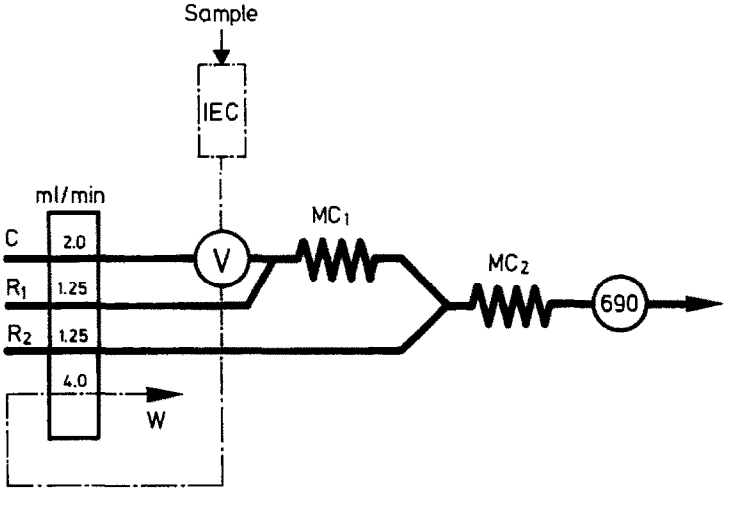

Fig. 1. Flow manifold used in the investigation of sensitive determination of arsenate, arsenite and sum of both ions. The dashed line represents the additionally installed anion-exchange microcolumn (IEC) used to separate arsenite from phosphate, arsenate and silicate. The dimensions of the first mixing coil are 60 and 120 cm length, respectively, when used without and with on-line oxidation (see text for further explanations). The second reaction coil was 60 cm in both cases. V, Injection valve; W, waste.

Chemicals and solutions

All chemicals were of analytical grade quality. Bidistilled water was used throughout. Carrier and reagent solutions were degassed by means of water vacuum pump. Standard solutions were prepared by appropriate dilution of stock solutions containing 1 g/l. arsenic as arsenate, phosphorus as phosphate and silicium as silicate, respectively (Merck Titrisol). The arsenite stock solution (0.1 g/l. arsenic) was prepared by reduction of arsenate standard using potassium iodide and ascorbic acid.[7] Completeness of reduction was assertained by the absence of reaction of a 10 mg/l. standard solution with molybdate (*i.e.* no Molybdenum Blue was formed in the assay[10]).

The reagent solutions for flow injection determination of arsenate were composed as follows: carrier stream was water. The acidic molybdate reagent (R_1 in Fig. 1) was prepared by dissolution of 5 g ammonium molybdate in 300 ml water. After addition of 17.5 ml concentrated sulfuric acid (Caution!) the solution was made up to 500 ml with water. The reduction solution (R_2 in Fig. 1) was prepared by addition of 14 ml concentrated sulfuric acid to 300 ml of water. To this solution 0.1 g stannous chloride and 1 g hydrazine sulfate were added and the solution made up to 500 ml with water.

For the flow injection determination of arsenite the acidic molybdate reagent (R_1 in Fig. 1) used for determination of arsenate was modified in that potassium permanganate was added to give a final concentration of $10^{-4}M$ in the reagent mixture.

Ion exchange materials used were strongly alkaline anion exchangers IRA-900 and IRA-904 (Rohm & Haas), Lewatit M 500 and MP 500 (Bayer) and Dowex 1-X8 (Bio-Rad). Prior to use all materials were converted into the chloride form by repeated washings with sodium chloride solution (10 g/l.) and thorough rinsing with water. The ion-exchangers were slurry filled into the perspex columns. Care was taken to achieve a tight packing and to prevent gas-bubble inclusions.

RESULTS AND DISCUSSION

Flow injection determination of arsenate by Molybdenum Blue method

Only two papers have been published[20,21] on flow injection determination of arsenate by the Molybdenum Blue method. It is, however, well known[10–15,22–24] that arsenate interferes strongly in the determination of phosphate using the same method so that it can be assumed that procedures developed for the determination of phosphate are applicable to arsenate determination, too. The experimental conditions used in the various papers on arsenate and phosphate determination by FIA differ considerably with respect to reagent concentrations, acidity of the assay and choice of the reducing agents. A sensitive and well-established method for phosphate[22] which has also been used for years in our laboratory was adopted for the present purpose. In initial measurements the reagent compositions were taken as described[22] without further optimization (see Experimental). It became evident that the reaction kinetics for arsenate are very similar to that of phosphate. By using tin(II) chloride as reducing agent the commonly employed antimony catalyst can be omitted and almost full development of colour achieved within the time available in fast FIA measurements. Length of mixing coils, injection volume and flow rates were optimized by the univariant method. Though high sensitivity was the major goal analysis time, reagent consumption and baseline stability (noise and drift) were also taken into account. The final flow system used is depicted in Fig. 1. The injection volume was set to 500 μl in all measurements. With this set-up arsenate determination is possible within the concentration range 5–500 μg/l. arsenic as arsenate giving linear calibration plots ($A = 1.14$ l./mg $+ 0.0024$). The detection limit (3σ) was 1.7 μg/l. As (3.1 μg/l. arsenate). The precision of repetitive measurements within the concentration range was generally better than 5% relative standard deviation (RSD).

In order to examine the degree of interference of phosphate and silicate various concentrations of these ions alone and together with arsenate were measured. Under the conditions used silicate was found not to interfere up to a concentration of 10 mg/l. Si which is in reasonable agreement with earlier findings for phosphate determination.[22,25] Above this value the interference was still low, 50 mg/l. silicium giving a signal equivalent to 18 μg/l. arsenic. The interference of phosphate, however, was severe. The relative response factor, *i.e.* relation between the slope of the calibration plots of arsenate and phosphate on the basis of equimolar solutions was 0.82. This value is slightly higher than previously reported values.[13,20,22]

Determination of sum of arsenate and arsenite

Since arsenite does not form a heteropoly acid with molybdate, total arsenic can only be determined after oxidative sample pretreatment.[10] In the present study several oxidizing agents, including cerium (IV), hydrogen peroxide, permanganate, iodine and iodate have been examined. The criteria for suitability of the oxidizing agent are completeness of oxidation in a reasonably short time and no interference in the spectrophotometric determination of arsenate thus formed. Completeness of reduction was evaluated by comparison of response of equimolar arsenite and arsenate standard solutions.

Artefact signals due to color or refractive index changes as well as formation of gas bubbles (in the case of hydrogen peroxide) occurred in several instances when samples pretreated with sufficiently high concentrations of oxidizing agent were injected into the manifold shown in Fig. 1. These effects could be partially overcome by installation of an additional flow channel carrying the oxidizing agent and merging the carrier stream prior to the addition of R_1 in Fig. 1. However, slow reaction kinetics and increasing baseline fluctuations were observed with several oxidizing agents. Permanganate proved to be most suitable since oxidation of arsenite is instantaneous; the permanganate colour disappears when tin(II) chloride solution is merged (R_2 in Fig. 1) and it can be directly added to R_1 omitting a fourth flow channel. The concentration of permanganate in R_1 must be sufficiently high to provide an excess over the sum of species oxidizable by permanganate at given experimental conditions. For well-water analysis, with chemical oxygen demands typically below 5 mg/l., a concentration of $10^{-4}M$ permanganate in R_1 was found sufficient. This change in the composition of R_1 did not require an increase of the tin(II) chloride concentration in R_2 which, however, became necessary if considerably higher permanganate concentrations are used; *i.e.* part of the tin(II) is consumed by the excess of permanganate. The performance of the method with respect to working range, slope of the calibration curve, precision and the interference of silicate and phosphate did not show significant differences to that found in the determination of arsenate (see above).

Separation of arsenite

As mentioned above phosphate strongly interferes in the determination of arsenate by the Molybdenum Blue method. Separation of these two species is possible by liquid extraction procedures,[10,14,15,25] ion chromatography[26] and has also been done in FIA using ion-exchange minicolumns.[21] Since the present work aimed to selectively determine arsenite, its separation from phosphate and arsenate had to be accomplished. Commonly this has been done by gas-phase separation of volatile arsine,[8,10,27] liquid–liquid extraction of arsenite[8,10,28,29] or chromatographic separation techniques.[30–34] More recently, solid phase extraction of arsenic (III) complexes has been used for selective separation and preconcentration of arsenite.[35,36] Another route which is proposed in the present work is the removal of phosphate and arsenate from the sample solution by anion exchange separation followed by the determination of non-retained arsenite. To prevent arsenite also being removed its amphoteric character is utilized. With a pK_A-value of 9.2 arsenious acid [(described as H_3AsO_3, $HAsO_2$ or As (III)] exists in solution as a neutral or cationic species at medium to low pH. Arsenate, however, with dissociation constants of pK_1 2.3, pK_2 6.8 and pK_3 11.6 exists primarily as anionic species in neutral and low acidic medium. Accordingly, there is a reasonably large pH-window where separation of the two species by means of anion exchange should be feasable.[37] Experimental evidence can also be found in several papers on anion exchange chromatographic separation of arsenate and arsenite where large differences in the capacity factors of the two species occur.[30–32] Retention of arsenite has, however, been observed in several instances in spite of the fact that the specie is not ionized at the pH-values of the eluents used.[33,37]

Our studies on the retention behaviour of arsenite on strong anion exchangers were made by continuously pumping arsenite solutions through the microcolumns and analysis of the effluent by the FIA-method developed for determination of the sum of arsenite and arsenate (see above). Comparison between signals obtained without passing the arsenite through the column thus gives evidence for any retention of arsenite. Recovery studies for arsenite within the concentration range 10–500 μg/l. at variable pH for all anion exchange materials investigated revealed complete recovery, *i.e.* no retention on the column, when the sample pH was in the range 2–4. At higher pH values the recovery of arsenite was diminished. Lower pH values were

not investigated since arsenate was thought to be not fully retained (pK_1 2.3).

The strong affinity of phosphate and arsenate to strong alkaline anion exchange materials[38] allows the effective removal of these ions even in the presence of high concentrations of accompanying anions. In batch experiments the exchange capacity was determined and the influence of other anions on the efficiency of removal was investigated for different ion exchangers (see Experimental). Dowex 1-X8 was found to offer the highest capacity (*ca.* 1.4 mequiv/ml)[39] and, additionally, fast exchange kinetics which are desirable for column applications.

For the actual application in FIA the minicolumn filled with Dowex 1-X8 (*ca.* 700 μl wet volume) was installed in the sample aspiration line as shown in Fig. 1 (dashed lines). By this means the effluent from the column feeds the injection loop and can be successively injected into the FIA-system. The minimal volume necessary to ensure that the loop is filled with new sample is 800 μl plus the volume of the loop. In practice with 500 μl injection volume at least 2 ml were aspirated prior to injection. After each experiment the microcolumn was regenerated with 2 ml 0.5*M* sodium chloride solution and rinsed with 5 ml water. In order to prevent the aspiration of air during change from sample to regeneration and washing solutions the pump was intermittently stopped for few seconds. By using a three-way valve this measure can be omitted and would ensure a fully automatic procedure.

Breakthrough experiments were performed with different concentrations of phosphate and arsenate at various aspiration rates. With a limit of determination of 2.4 and 4.5 μg/l. for phosphorus and arsenic, respectively, any breakthrough could be sensitively detected. It was found that over a wide concentration range removal of both anions was complete as long as the aspiration rate did not exceed 4 ml/min and the exchange capacity of the column (*ca* 10 mg dihydrogen phosphate, which is the predominant species at pH around 4) is not approached. Given a maximum phosphate concentration of 10 mg/l. this theoretically corresponds to 50 l. (!) of sample solution. At higher flow rates, however, phosphate was not fully retained even if the exchange capacity is far from being reached (kinetic breakthrough). Arsenate behaved in a very similar way.

The effect of other anions on the removal efficiency of phosphate and arsenate was also investigated. It was found that up to 5 g/l. (higher values not tested) chloride and nitrate had no influence on phosphate and arsenate retention. Sulphate at concentrations above 1 g/l., however, led to decreased retention which is obviously due to competition, *i.e.* sulphate is likewise strongly retained as phosphate and arsenate and occupies ion exchange sites.

Selective determination of arsenite. Performance characteristics and calibration data

The manifold shown in Fig. 1 (dashed lines) was applied for the selective determination of arsenite. As mentioned above, phosphate and arsenate are effectively removed by anion exchange and arsenite passing through the column can be determined by the Molybdenum Blue method following in-line oxidation by permanganate in the first reaction coil.

To prove the suitability of the method, pure arsenite standards and a series of mixed solutions containing various amounts of arsenite, arsenate and phosphate were analyzed. All solutions were adjusted to pH 2–4 by addition of few drops of hydrochloric acid. The linear working range for arsenite was found to be 5–800 μg/l. arsenic ($A = 1.23$ l./mg $- 0.0018$). The limit of detection (3σ) was 1.2 μg/l. As (1.7 μg/l. AsO_2^-). The relative standard deviations ($N = 10$) for the determination of 10 and 500 μg/l. arsenic were 2.3 and 1.8%, respectively. Higher concentration levels were easily accessible by the use of smaller injection volumes.

At given experimental conditions the sample residence time within the manifold amounted to less than 1 min. Since a new sample can be aspirated through the microcolumn and loaded into the injection loop while the previous one is processed, an injection frequency of 50 per hr is realistically achievable. Taking into account that samples are generally injected at least twice and some time is spent to regenerate the microcolumn, the sample throughput is about 20 per hr.

Results obtained in the analysis of arsenite standards in the presence of potentially interfering anions are given in Table 1. As can be seen, the recovery of arsenite ranged from 95 to 104% demonstrating efficient elimination of phosphate and arsenate over a wide range of concentration ratios between analyte and interfering ions. It is also obvious that the precision of the method was not affected by the presence of accompanying ions.

Table 1. Recovery of arsenite standards in the presence of various amounts of phosphate, arsenate and silicate

Arsenite given ($\mu g/l.$)	Concentration of interfering ions* ($mg/l.$)	Mean of found arsenite† ($\mu g/l.$)	Recovery (%)
10	0.1 As; 0.1 P; 10 Si	9.56	95.6 ± 1.7
10	0.5 As; 1.0 P; 10 Si	9.92	99.2 ± 3.4
10	1.0 As; 5.0 P	10.0	100.0 ± 4.3
20	2.0 P; 10 Si	19.4	97.0 ± 2.4
50	2.0 P; 10 Si	49.9	99.8 ± 5.2
50	0.5 As; 2.0 P; 10 Si	48.3	96.6 ± 3.8
100	0.1 As; 0.5 P	98.8	98.8 ± 2.5
100	0.5 As; 1.0 P	103.5	103.5 ± 4.4
100	0.5 As; 2.0 P; 10 Si	102.1	102.1 ± 5.1
100	0.5 As; 5.0 P; 10 Si	98.0	98.0 ± 3.6
500	0.5 As; 1.0 P	487.3	97.5 ± 1.7
500	0.5 As; 5.0 P; 10 Si	495.3	99.1 ± 3.8
500	0.5 As; 10 P	508.2	101.6 ± 2.2

*All samples were analyzed using the manifold shown in Fig. 1 (dashed line). Concentrations given are for arsenic, phosphorus and silicium as arsenite, arsenate, phosphate and silicate, respectively.

†Data are based on repetitive measurements of five individual samples.

Determination of arsenite in real water samples

The results of analysis using the proposed procedure of several water samples with and without added arsenite are shown in Table 2. The water samples after collection were acidified to pH 2–4 by dropwise addition of hydrochloric acid. The sample solution then was continuously aspirated through the anion-exchange microcolumn and after passage of at least 2 ml the effluent was injected into the manifold (see Fig. 2). Successive injections of the same sample (usually 2–5 repetitions) were made without intermediate regeneration of the microcolumn. However, prior to aspiration of a new sample the column was regenerated as described above. The results summarized in Table 2 show that only one sample (surface water S3) contained measurable arsenite. The recovery of added arsenite was almost 100% in all cases and the precision obtained reveals excellent performance of the proposed method. The efficient

Table 2. Determination of arsenite in water samples

Sample	Arsenite added* ($\mu g/l.$)	Phosphate added* ($mg/l.$)	Arsenite found* ($\mu g/l.$)	Recovery† (%)
Berlin tap water/S1	5	—	5.4	108.0
	10	—	9.7	97.0
	40	—	41.3	103.3
	100	—	96.8	96.8
Berlin tap water/S2	10	—	10.6	106.0
	10	0.5	9.4	94.0
	10	1.0	10.8	108.0
	50	2.0	48.3	96.6
Landwehrkanal/S3	—	—	4.6	—
	10	—	15.3	107.0
	10	1.0	14.5	99.0
	10	5.0	15.8	112.0
	50	1.0	56.0	102.8
	100	—	100.7	96.1
	100	5.0	103.0	98.4
River Spree/S4	10	1.0	9.1	91.0
	10	5.0	10.3	103.0
	50	5.0	49.2	98.4
	100	5.0	94.9	94.6
Mineral water/S5	10	—	10.2	102.0
	10	0.5	9.5	95.0
	50	1.0	48.6	97.2

Various amounts of arsenite and phosphate were added to the samples prior to analysis using the manifold shown in Fig. 1 (dashed line).

*Concentrations given refer to arsenic and phosphorus.

†Data given are correct for blank or arsenite values found in the unspiked samples.

removal of phosphate likely to be present in real water samples was cross-checked by addition of phosphate to some of the samples. No interference was encountered (see Table 2).

CONCLUSIONS

The development of a selective and sensitive spectrophotometric method for determination of arsenite in water has been presented. It involves the anion-exchange separation of interfering ions, *i.e.* phosphate, arsenate and silicate, following oxidation of unretained arsenite to arsenate and detection of Molybdenum Blue formed in a two-step reaction scheme. Using the flow injection approach the multistage procedure is performed without manual interaction. Sample processing occurs at reasonably high throughput with high precision and reliability. Automatization of the method can be easily achieved.

REFERENCES

1. J. F. Ferguson and J. Gavis, *Water Res.*, 1972, **6**, 1259.
2. *Medical and Biological Effects of Environmental Pollutants: Arsenic.* National Academy of Sciences, Washington DC, 1977.
3. World Health Organization *Environment Health Criteria. 18. Arsenic*, p. 174. WHO, Geneva, 1981.
4. Y. Talmi and C. Feldman, The determination of traces of arsenic—a review, in *Arsenical Pesticides*, E. A. Woolson (ed.). American Chemical Society, Washington DC, 1975.
5. W. Holak, *Anal. Chem.*, 1969, **41**, 1712.
6. R. K. Anderson, M. Thompson and E. Culbard, *Analyst*, 1986, **111**, 1143.
7. Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, DIN 38 405, Teil 18. Beuth, Berlin, 1985.
8. J. Minczewski, J. Chwastowska and R. Dybczynski, *Separation and Preconcentration Methods in Inorganic Trace Analysis.* Ellis Horwood, Chichester, 1982.
9. H. Ohashi, H. Kawaguchi and K. Yamamoto, *Anal. Chim. Acta*, 1979, **111**, 301.
10. H. Onishi, Photometric Determination of Traces of Metals, in *Chemical Analysis*, D. J. Elving and J. D. Winefordner (eds), Vol. 3, Part II A. John Wiley, New York, 1990.
11. R. Kuroda, I. Ida and K. Oguma, *Mikrochim. Acta*, 1984, **I**, 377.
12. R. E. Stauffer, *Environ. Sci. Technol.*, 1980, **14**, 1475.
13. M. Lopez Carreto, D. Sicilia, S. Rubio and D. Perez-Bendito, *Anal. Chim. Acta*, 1993, **283**, 481.
14. A. G. Fogg, D. R. Marriott and D. T. Burns, *Analyst*, 1972, **97**, 657.
15. E. M. Donaldson, *Talanta*, 1977, **24**, 105.
16. J. Ruzicka and E. H. Hansen, *Flow Injection Analysis*, 2nd Ed. John Wiley, New York, 1988.
17. M. Valcarcel and M. D. Luque de Castro, *Flow Injection Analysis—Principles and Applications.* Ellis Horwood, Chichester, 1987.
18. G. D. Clark, D. A. Whitman, G. D. Christian and J. Ruzicka, *Crit. Rev. Anal. Chem.*, 1990, **21**, 357.
19. D. D. Luque de Castro and M. Valcarcel, *Anal. Chim. Acta*, 1992, **261**, 425.
20. P. Linares, M. D. Luque de Castro and M. Valcarcel, *Anal. Chem.*, 1986, **58**, 120.
21. Y. Narusawa, *Anal. Chim. Acta*, 1988, **204**, 53.
22. Application Note AN 60, Determination of orthophosphate based on the stannous chloride method using flow injection analysis, Tecator AB, Höganäs, 1981.
23. Water Quality—Determination of Phosphorus. Part 1: Ammonium Molybdate Spectrometric Method. ISO 6878/1, 1986.
24. P. J. Worsfold, J. R. Clinch and H. Casey, *Anal. Chim. Acta*, 1987, **197**, 43.
25. W. R. Nall, *Analyst*, 1971, **96**, 398.
26. J. Weiß, *Ionenchromatographie*, pp. 86, 367. Verlag Chemie, Weinheim 1991.
27. H. Onishi and E. B. Sandell, *Mikrochim. Acta*, 1953, **I**, 34.
28. G. O. Brink, P. Kafalas, R. A. Sharp, E. L. Weiss and J. W. Irvine, *J. Am. Chem. Soc.*, 1957, **79**, 1303.
29. D. Chakraborti, K. J. Irgolic and F. Adams, *J. Assoc. Off. Anal. Chem.*, 1984, **67**, 277.
30. A. A. Grabinski, *Anal. Chem.*, 1981, **53**, 966.
31. G. R. Ricci, L. S. Shepard, G. Colovos and N. E. Hester, *Anal. Chem.*, 1981, **53**, 610.
32. J. Aggett and R. Kalwani, *Analyst*, 1983, **108**, 1495.
33. E. H. Larsen and S. H. Hansen, *Mikrochim. Acta*, 1992, **109**, 47.
34. A. G. Howard and L. E. Hunt, *Anal. Chem.*, 1993, **65**, 2995.
35. J. T. Van Elteren, G. J. M. Gruter, H. A. Das and U. A. Th. Brinkman, *Int. J. Environ. Anal. Chem.*, 1990, **43**, 41.
36. M. Sperling, X. Yin and B. Welz, *Spectrochim. Acta*, 1991, **46B**, 1789.
37. P. Schramel and L. Xu, *Fresenius, J. Anal. Chem.*, 1992, **343**, 373.
38. K. Dorfner, *Ion Exchangers.* Walter de Gruyter, Berlin, 1990.
39. C. Hänsel, Diploma Thesis. Technical High School Berlin, 1993.