

Determination of iron and manganese in mineral waters of Galicia (Spain) by atomic absorption spectrophotometry

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Abstract

This paper describes the determination of Fe and Mn in thirty-six mineral waters of Galicia (NW Spain) by means of atomic absorption spectrophotometry (AAS) with an air/acetylene flame. In most cases iron was determined without modifying its concentration after checking its oxidation state *in situ*. Manganese was determined after concentration by evaporation. Recovery and reproducibility are good. In almost all samples the Mn/Fe ratio lies between 0,05 and 0,20.

Introduction

This paper is the latest in a series of reports (González-Portal *et al.*, 1981 and 1985) on the mineral waters of Galicia (NW Spain). These waters run through large masses of granite, gneiss, porphyry and diabasic rock which are in places overlain by paleozoic sediments. Beds of schist and calcareous deposits are also found as well as fissures and rifts filled with metal sulphides and iron oxides. The resulting mineral waters contain sodium bicarbonate, alkaline silicates and soluble sulphides. The continuous release of carbon dioxide saturates the water and favours the dissolution of iron oxides, making most of the springs in this region ferruginous (Iglesias-Iglesias, 1924).

The popularity of atomic absorption spectroscopy (AAS) for environmental analysis, and in particular for the analysis of water, is reflected by the large amount of significant research in this field, including interlaboratory studies (McFarren and Lishka, 1968; McClellan, 1975; Smythe and Finlayson, 1978; Neitzert and Lieser, 1979; Smith, 1979; Sutton *et al.*, 1979; Miles and Cook, 1981), annual reviews (Annual Reports on Analytical Atomic Spectroscopy, 1971-83; WPCF, 1976-83) and other important contributions (Omang, 1971; Pickford and Rossi, 1972; Slavin, 1980; Sourova and Capkova, 1980; Analytical Chemistry, 1981). Atomic Absorption Spectrophotometry (AAS) is ideal for the determination of metals in mineral waters (APHA *et al.*, 1976) due to its simplicity, rapidity, specificity, accuracy and precision, and was consequently rapidly adopted as a standard method by the ASTM (ASTM, 1979) and the American Public Health Association (APHA *et al.*, 1976). Iron and manganese are determined in natural waters by AAS using an air/acetylene flame. Although the detection limit for manganese is fairly low (0,005 $\mu\text{g/ml}$) (McClellan, 1975) it is in general necessary to concentrate samples using a variety of procedures, such as instrument evaporation (Department of the Environment and National Water Council (UK), 1983; The Severn Estuary Chemists' Subcommittee, 1984; Webster and Wood, 1984), ion exchange (Aldous *et al.*, 1975; Brodtmann and Houghton, 1975) or complexation/extraction with reagents such as ammonium pyrrolidone dithiocarbamate/methyl isobutyl ketone (APDC/MIBK) (Bone and Hibbert, 1979; Rasmussen, 1981). In the case of manganese, the complexes formed in the latter method are unstable, and the reproducibility of the results is poor (Yanagisawa *et al.*, 1968). After preconcentration of samples, quantities of the order of a nanogram of iron and manganese can be determined by atomic absorption spectrophotometry.

This paper describes the use of AAS with an air/acetylene flame, to determine iron and manganese in samples of Galician mineral waters collected directly from the springs. The values obtained for iron compared favourably with those found using the standard 1,10-phenanthroline method (APHA *et al.*, 1976).

Experimental

Reagents

Nitric acid, Merck AR (d = 1,42)
Hydrochloric acid, Merck AR (d = 1,19)
Ammonium thiocyanate, Merck (1 % solution)
Iron standard, Merck Titrisol, containing 1 000 mg/l of Fe. Solutions containing 0,5; 1,0; 2,0; 3,0 and 5,0 mg/l were prepared by dilution.
Manganese standard, Merck Titrisol, containing 1 000 mg/l of Mn. Solutions containing 0,1; 0,2; 0,3; 0,4; 0,5 and 0,6 mg/l were prepared by dilution.
Hydroxylamine hydrochloride, Merck AR (10 % solution)
1,10-Phenanthroline, Merck AR (0,1 % solution)
Ammonium acetate buffer, was prepared by dissolving 250g of ammonium acetate (Merck AR) in 150 ml of distilled water, adding 700 ml glacial acetic acid, diluting to 1 litre distilled water and bringing the pH to 3,2 to 3,3.

Apparatus

Perkin-Elmer model 303 atomic absorption spectrophotometer equipped with single-element lamps, pre-mix chamber, standard burner (Ref. 0040-0266) and Hitachi Perkin-Elmer model 165 recorder.
Bausch and Lomb "Spectronic 700" VIS-UV spectrophotometer equipped with glass cells with a 10 mm light path.
Beckman Electromate pH-meter equipped with electrodes sensitive to $\pm 0,02$ pH units.
A 250V/500W quartz infrared (IR) radiator.

Sample collection and screening

Thirty-six Galician mineral springs were chosen for sampling on the basis of their historical, therapeutical or possible commercial interest. Samples were collected and stored following standard procedures (APHA *et al.*, 1976).

The oxidation state of iron and manganese in natural waters depends on the redox character of the medium (Hariya *et al.*, 1964; Ostapenya and Mikhailik, 1974; Rumynin and Golovina, 1979)

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(Fig. 1). In the present study samples were screened *in situ* for iron (III) using a plate test with 1 % (m/v) ammonium thiocyanate as reagent (Vogel, 1945). Only 5 of the samples gave a positive result to the test [which is sensitive to 0,25 µg of iron (III)], and it was concluded that all the iron in most of the samples was present as Fe (II).

Procedure

Sample aliquots of 100 ml were acidified with 10 % (v/v) nitric acid and heated to boiling point to eliminate all dissolved gases. For the determination of iron, 8 samples required dilution, 4 concentration, and the remainder were analysed without modification of their concentration. For the determination of manganese, all but 3 samples were concentrated by infrared evaporation.

Once the hollow cathode lamp of the spectrophotometer had been stabilised, the atomic absorption spectrophotometry settings in each case were as follows:

	Fe	Mn
Hollow cathode lamp		
Lamp current (mA)	20	15
Wavelength (nm)	248,3	279,6
Observation height above burner (mm)	11,0	14,0
Air pressure (kg/cm ²)	0,57	0,66
Acetylene pressure (kg/cm ²)	0,28	0,59
Sample uptake rate (ml/min)	2,0	3,0

The absorbance of the standard solutions was determined immediately before those of the samples.

Iron was also determined by VIS-UV spectrophotometry using 1,10-phenanthroline (APHA *et al.*, 1976).

Reproducibility, accuracy and recovery

The dissolved salt content of these waters ranges from 0,129 to 2 220 mg/l. The reproducibility of the analytical results was studied using solutions of distilled water containing the average concentration (500 mg/l) of the commonest salts (potassium and sodium chlorides). Aliquots of iron and manganese standards were added before analysis, the solutions being analysed five times. Recovery tests were conducted in the usual manner.

Results and discussion

The concentrations of iron and manganese found in the Galician mineral waters are given as frequency histograms in Figs. 2a and 2b. The European Economic Community (EEC) maximum admissible limits are also shown in the histograms.

TABLE 1
COMPARISON OF IRON CONCENTRATIONS AS FOUND BY
AAS AND PHENANTHROLINE METHODS

Water samples	Iron (mg/l)		Difference (D)
	AAS	1,10-phenanthroline	
A	0,17	0,12	-0,05
B	0,14	0,10	-0,04
C	0,14	0,10	-0,04
D	0,15	0,10	-0,05
E	0,15	0,14	-0,01
F	0,13	0,08	-0,05
G	0,15	0,10	-0,05
H	0,32	0,30	-0,02
I	0,41	0,40	-0,01
J	0,60	0,60	0,00
K	0,79	0,65	-0,06
L	2,37	2,33	-0,04
M	5,60	6,02	+0,42
N	5,70	5,95	+0,25
O	10,68	10,82	+0,14

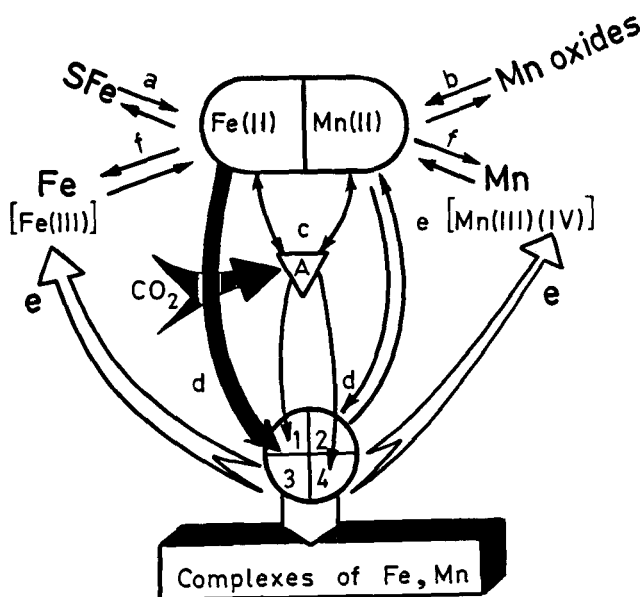


FIGURE 1

Relevant chemical pathway of iron and manganese in waters

- A - Microbial biomass.
- a - FeS decomposition.
- b - Mn oxides decomposition
- c - Immobilisation of iron and manganese.
- d - Complexation of Fe and Mn (pH = 7 or > 7).
- e - Mineralisation
- f - Fe and Mn oxidation
- 1 - Iron soluble (Fe(HCO₃)₂; FeSO₄; Fe(OH)₂ and humic complexes).
- 2 - Manganese soluble (MnCO₃).
- 3 - Iron insoluble
- 4 - Manganese insoluble

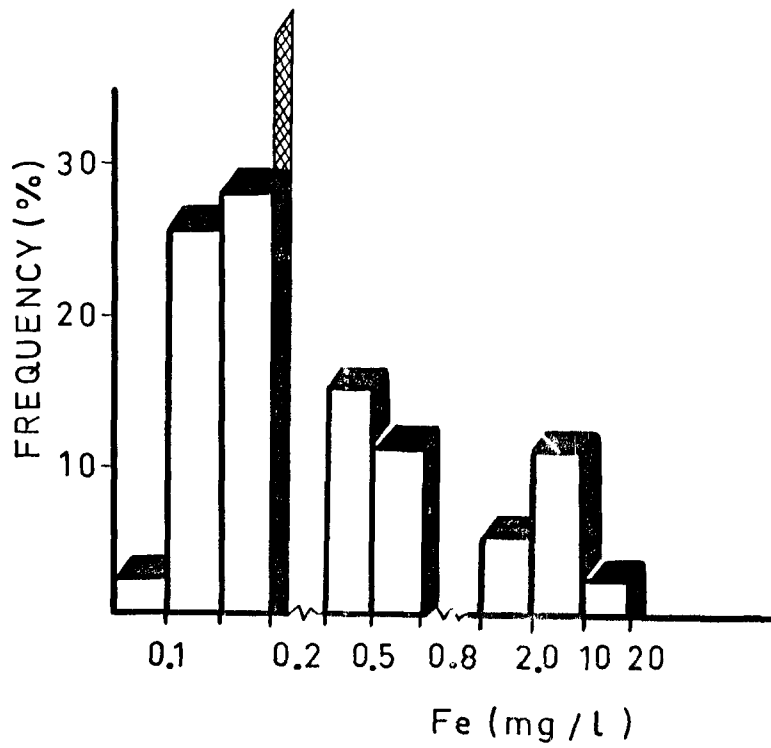
The comparison of iron determined by the two methods employed is statistically compatible with the null hypothesis of there being no difference between the mean of the results for the AAS and phenanthroline methods (Table I). Fisher's "t" for the 14 degrees of freedom and a 95 % confidence level is 2,145 as compared to a "t" value for the differences of 0,720. The greatest discrepancies arise in the 0,1 to 0,2 mg/l concentration range, where the AAS method gave slightly lower concentrations than those found with the phenanthroline method.

The recovery for iron was in the range 99,0 to 101,7 % and recovery for manganese in the range 93,0 to 97,5 %. Accuracy was therefore acceptable.

The test for precision showed that the percentage relative error (% RE) for 95 % confidence interval for Fe was 3,0 % or less for Fe concentrations of 1 mg/l and higher, and 9 % for an Fe concentration of 0,5 mg/l. For Mn the % RE was 3,2 % or less for Mn concentrations of 0,30 mg/l and higher, and 6,6 % for a Mn concentration of 0,1 mg/l.

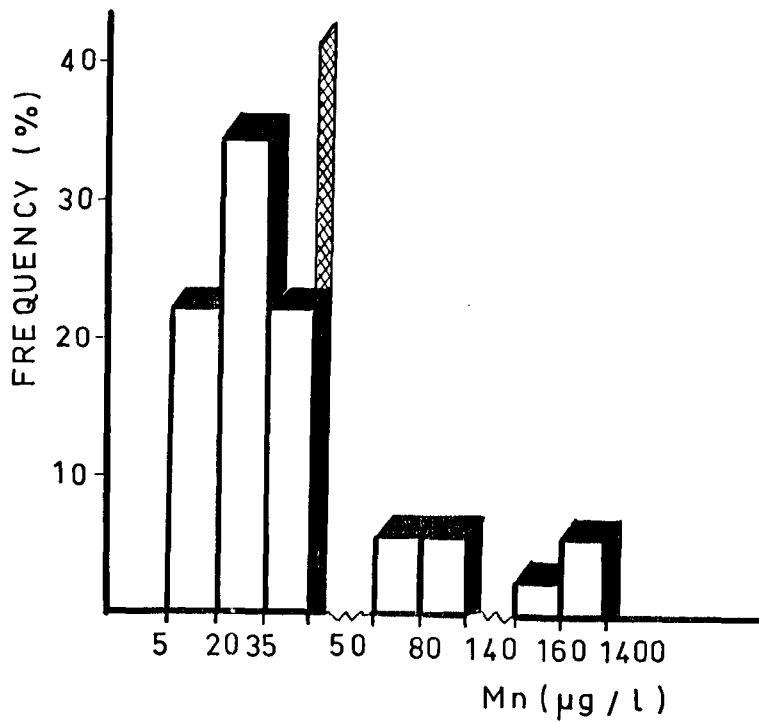
The manganese/iron ratio of all samples is in the range 0,05 to 0,27 regarded by Plochniewski (1972) as typical of Jurassic and Cretaceous waters. Two samples of prequaternary origin lie outside this range (Table II).

The values of iron and manganese found in the present study agree with published values (Table III) and are consistent with



IRON (The EEC maximum admissible limit of 0,20 mg/l is shown cross-hatched).

FIGURE 2
Histograms showing frequency of occurrence of iron and manganese in mineral waters of Galicia.



MANGANESE (The EEC maximum admissible limit of 50 µg/l is shown cross-hatched).

these waters' origin in deep Cretaceous and Tertiary strata, composed of schists, gneiss, volcanic rocks and clay. The presence of iron (II) is consistent with the therapeutical use of most of these waters during the past century. These waters were studied in the nineteenth century by A. Casares-Rodriguez, who determined iron and manganese oxides gravimetrically (Casares-Rodriguez, 1837; Maiz-Eliezgui, 1952). The only recent analysis of these waters refers to the springs of Cuntis (López de Azcona, 1974).

Conclusion

Atomic absorption spectrophotometry proves to be the most rapid, accurate and precise method for the determination of iron and manganese in mineral spring waters of Galicia in NW Spain. Iron content varied from zero to 10,4 mg/l and manganese content from 5,6 to 1 400 µg/l.

TABLE II
IRON AND MANGANESE CONTENT OF THE MINERAL WATERS STUDIED

Number of springs	Hardness(*)	Type of water and mineral content(**)	Range Fe (mg/l)	Range Mn (µg/l)	Ratio Mn/Fe
7	10-15	Very soft	0,10-0,17	8,6-38,7	0,05-0,27
1	7	Soft (40-200)	0,08-1,70	16,8-63,3	0,01-0,22
10	15-30	Very soft (200-500)			
3	20-30	Very soft			
3	30-40	Soft (500-1 000)	0,13-0,19	10,0-66,7	0,08-0,40
3	40-70	Soft (< 1 000)	0,20-0,41	22,5-66,7	0,06-0,24
4	140-270	Medium-hard (> 1 000)	0,15-2,37	15,3-55,0	0,02-0,15
2	270-400	Hard (High content)	0,60-0,79	28,7-30,0	0,04-0,05
1	930	Very hard (High content)	10,68	33,3	-
2	< 3 000	Salts waters (> 3 000)	2,83-5,60	6x10 ² -14x10 ²	-

(*) Hardness expressed as mg/l of CaCO₃

(**) Mineral content in parenthesis is expressed as mg/l.

TABLE III
SOME LEVELS OF IRON AND MANGANESE IN WATERS

Origin	Geological era	mg/litre	
		Fe	Mn
GERMANY (Schneider and Roeder, 1978) (a)	-	0,02-1,0	0,02-1,0
JAPAN (Itoyana, 1971)	-		
Deep well A	-	2,07	0,44
Deep well B	-	12,80	1,61
NEW ZEALAND (Goguel, 1977) (b)	-	0,005	0,001
POLAND (Plochowski and Pich, 1966)			
"	Primary (Paleozoic)	0,0-1 000	0,2-20,0
"	Secondary (Mesozoic)	0,0-1 000	0,2-20,0
"	Secondary (Cretaceous)	2,0	0,1
Deposits delta	Quaternary	5,0	0,1-2,0
Terrace formation	Quaternary	0,3-5,0	0,1
USSR (Serezhnikov, 1978)			
Volcanic rock (c)	-	-	0,03-5,0
(400-2 200 mg/l Mn) (d)	-	-	0,08-0,1
USSR (Belorussian) (Ostapenya and Mikhailik, 1974)			
"	Tertiary	4,0	-
"	Quaternary	18,0	-
USA (Tennessee) (Wilson, 1967)			
Aquifers {Sewanee (e)	-	0,05-5,0	0,0-0,9
{Rockcastle (f)	-	0,2-2,8	0,2-0,8
(a) Drinking waters	(b) Geothermal waters		
(c) Subsurface waters	(d) Surface waters		
(e) Rocks (%) = 0,61 Fe and 0,39 Mn	(f) Rocks (%) = 1,23 Fe and 1,64 Mn		

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- ALDOUS, K.M., MITCHELL, D.G. and JACKSON, K.W. (1975) Simultaneous determination of seven trace metals in potable water using a vidicon atomic absorption spectrometer. *Anal. Chem.* **47** 1 034.
- Analytical Chemistry* (1981) The biennial review of water **53** 182R.
- Annual Reports on Analytical Atomic Spectroscopy* (1971-1984), Reviewing. The Royal Chemical Society, London.
- APHA, AWWA, WPCF (1976) *Standard Methods for the Examination of Water and Wastewater*. 14th edition. Washington (USA) 38, 144, 207 and 224.
- ASTM (1979) *1979 Annual Book ASTM Standards*. American Society for Testing and Materials. Philadelphia, Pa (USA) 1 068-77 and 858-77.
- BONE, K.M. and HIBBERT, W.D. (1979) Solvent extraction with APDC and 2,6-dimethyl-4-heptanone for the determination of trace metals in effluents and natural waters. *Anal. Chim. Acta.* **107** 219.
- BRODTMANN, N.V. and HOUGHTON, I. (1975) Analytical determination of trace metals in water. *Water and Sewage Works* **122** 64-6.
- CASARES-RODRIGUEZ, A. (1837) *Análisis de las aguas minerales de Caldas de Reyes y Caldas de Cuntis*. Imp. V. é H. de Compañel. Santiago de Compostela (ESPAÑA). 59.
- CHAMYSHEVA, T.A., SHABONOVA, I.N., YUDELEVICH, I.G., SHEPAKOVA, I.R., GILBERT, E.N. and NIKITINA, V.P. (1981) Spectral and mass-spectrometric analysis of high-purity water with concentration of trace impurities by evaporation. *Khim. Tekhnol. Vody (USSR)* **3** 419 (C.A. (1982) **96** 74 359).
- Department of the Environment and National Water Council (UK) (1983). Iron and manganese in potable water by AAS: Tentative method 1983. *Methods Exam. Waters Associated Materials*, London. 20.
- GOGUEL, R. (1977) Improved analytical values for Al, Fe, Mn and Mg in Wairakei (New Zealand) geothermal waters. *New Z. Dep. Sci. Ind. Res. Bull.* **218** 27-30.
- GÓNZALEZ-PORTAL, A., BERMEJO-MARTINEZ, F. and BALUJA-SANTOS, C. (1981) *Análisis de las aguas minero-medicinales de Galicia*. Interpretación mineralógica. Paper presented at IIIst Congreso Iberoamericano del Medio Ambiente. Santiago de Compostela, June 23-26. 2-9.
- GÓNZALEZ-PORTAL, A., BALUJA-SANTOS, C. and BERMEJO-MARTINEZ, F. (1985) Calcium and magnesium analysis in mineral waters by AAS. XXIV Coll. Spectroscopicum International, Garmisch-Partenkirchen (Germany), 15-21 September.
- HARIYA, Yu., KIKUCHI, T. and MAKI, M. (1964) Data concerning the origin and precipitation processes of manganese dioxide. *Kobutsugaku Zasshi* **6** 368 (C.A., (1965) **63**, 11 164a).
- IGLESIAS-IGLESIAS, L. (1924) *Estudio Geológico de las fuentes minero-medicinales de Galicia*. Edited by Eco Franciscano. Santiago de Compostela. 26.
- ITOYAMA, T. (1971) Distribution of total iron and manganese in the piestic ground water at Takamatsu city, Shikoku Island. *Kogyo Yosui*, **152** 5 (C.A. (1972) **76** 49 683h).
- LOPEZ DE AZCONA, J.M. (1974) Manantiales minero-medicinales de Cuntis. *An. R. Acad. Farm.* **40** 395.
- MAIZ-ELEIZEGUI, L. (1952) Estudio bibliográfico del Dr. A. Casares-Rodriguez. *An. R. Acad. Farm.* (1) 29.
- MCCLELLAN, B.E., DEAN, J.A. and RAINS, Th.C. (1975) *Flame Emission and Atomic Spectrometry*. Edited by Marcel Dekker, New York. **3** 548.
- MCFARREN, E.F. and LISHKA, R.J. (1968) *Advances in chemistry Ser. 73. Trace Inorganics in water*. Edited by the American Chemical Society (USA). 253.
- MILES, D.L. and COOK, J.M. (1981) The interlaboratory ICP collaborative analysis programme for groundwater. XXII Coll. Spectroscopicum International, Tokyo (JAPAN), 4-8 September.
- NEITZERT, V. and LIESER, K.H. (1979) Multi-element standards for determination of trace elements in water by neutron activation. *Z. Anal. Chem.* **294** 28.
- OMANG, S.H. (1971) Practical application of flameless atomic absorption for the determination of nanogram amounts of metals. *Kjemi* **31** 13 (C.A. (1972) **76** 67 785x).
- OSTAPENYA, P.V. and MIKHAILIK, L.G. (1974) Natural factors specifically increasing the iron content in subsurface waters. *Probl. Okbr. Prir. Ispol's Stochykh Vod.* **40** Edited by Shlyapnikov, L.L. *Nauka i Tekhnika*. Minsk USSR (C.A. (1976) **85** 130 224s).
- PICKFORD, C.J. and ROSSI, G. (1972) Analysis of high purity water by flameless atomic-absorption spectroscopy. Part I. The use of an automated sampling system. *Analyst* **97** 647.
- PLOCHNIEWSKI, Z. and PICH, J. (1966) Iron and manganese in underground waters of various hydrogeochemical environments. *Kwart. Geol.* **10** 871-84. (C.A. (1968) **69** 61 426q).
- PLOCHNIEWSKI, Z. (1972) Iron and manganese in the subsurface waters in Pliocene, Miocene, Oligocene, Cretaceous and Jurassic sediments of the Polish lowlands. *Biml. Inst. Geol., Warsaw* **256** 5-37 (C.A. (1974) **81** 68 238m).
- RASMUSSEN, L. (1981) Determination of trace metals in sea water by Chelex-100 or solvent extraction techniques and atomic absorption spectrometry. *Anal. Chim. Acta.* **125** 117.
- RUMYNNIN, V.G. and GOLOVINA, N.G. (1979) Some characteristics of the formation of iron containing waters. *Izv. Vyssh. Uchebn. Zaved. Geol. Razved* **22** 106 (C.A. (1980) **92** 79 899f).
- SCHNEIDER, W. and ROEDER, R. (1978) Result of drinking water analysis-classical and with Technicon SMA System. *Auto Anal. Innovation: Problembesungen Med. Forsch. Ind., Dok. Vort. Technicon Symp.* **7th** 2 120-27 (1979) (C.A. (1981) **94** 36 000e).
- SEREZHNIKOV, A.I. (1978) Manganese in rocks and waters of the Koshelev volcanic massif region (Kamchatka). *Dokl. Akad. Nauk. SSSR* **238** 701 (C.A. (1978) **88** 139 855t).
- SLAVIN, W. (1980) The determination of trace metals in seawater *Atomic Spectroscopy* **1** 66-71.
- SMITH, R. (1979) Water analysis of South Africa: Interlaboratory comparison studies. Part V: Trace metal analysis. *Water SA* **5** (3) 128.
- SMYTHE, L.E. and FINLAYSON, R.J. (1978) Rapid spectroscopic methods for trace element investigations in natural waters. Australian Water Resources Council Technical Paper, No 32.
- SOUROVA, J. and CAPKOVA, A. (1980) Determination of trace elements in water with a high iron content by AAS. *Vodni Hospod.* **30** 133 (C.A. (1981) **94** 7 495).
- SUTTON, D.C., MORSE, R.S. LEGOTTE, P.A. and ROSA, W.C. (1979) Determination of ten selected trace metals in precipitation samples using atomic absorption and direct current plasma emission spectrometry. *Environ. Meas. Lab. Environ. Q. (US. Dept. Energy) EML-356*, 381-4.
- The Severn Estuary Chemists' Subcommittee* (1984) Results of an interlaboratory analytical quality control programme for non-saline waters. *Analyst* **109** 3.
- VOGEL, A.I. (1945) *A Text-book of Qualitative Chemical Analysis*. 3rd Edition. Longmans, Green and Co. London.
- WPCF (1976-1983). *Jour. Water Poll. Control Fed.* (Review Annual) **48-54**
- WEBSTER, J. and WOOD, A. (1984) Evaluation of an electrothermal atomisation procedure for the determination of lead in potable water. *Analyst* **109** 1 255.
- WHITFIELD, C.R. (1982) An interlaboratory analytical quality control exercise for total iron. *Anal. Newsl. (Water Research Centre)* (2) 11.
- WILSON, J.M. (1967) Iron and manganese in ground water from sandstone aquifers in Cumberland county Tennessee. *J. Tenn. Acad. Sci.*, **42** 104 (C.A. (1968) **68** 72 094k).
- YANAGISAWA, M., SUZUKI, M. and TAKBUCHI, T. (1968) Extraction of manganese dithiocarbamate complexes for atomic absorption spectrometry. *Anal. Chim. Acta.* **43** 500-502.