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 (Gônzalez-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 μg/m*l*) (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 pyrrolidine 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 m*l* of distilled water, adding 700 m*l* 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 ± 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 m*l* 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 (m*l*/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).

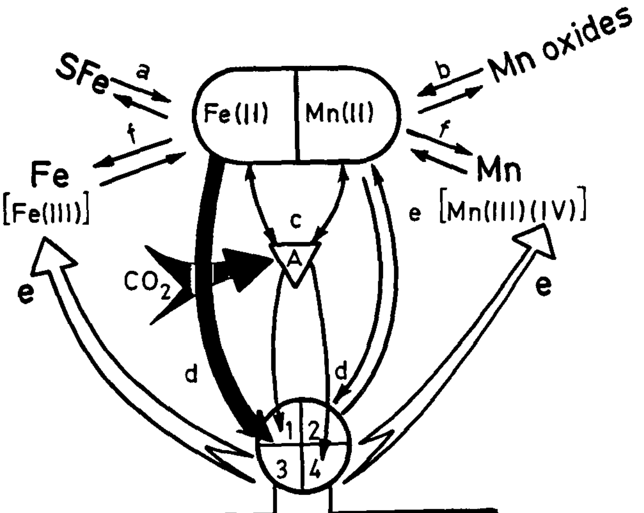


FIGURE 1

Relevant chemical pathway of iron and manganese in waters

A – Microbial biomass.
a – FeS decomposition.
b – Mn oxides decomposition
c – Inmobilisation of iron and manganese.
d – Complexation of Fe and Mn (pH – 7 or > 7).
e – Mineralisation
f – Fe and Mn oxidation
1 – Iron soluble ($Fe(HCO_3)_2$; $FeSO_4$; $Fe(OH)_2$ and humic complexes).
2 – Manganese soluble ($MnCO_3$).
3 – Iron insoluble
4 – Manganese insoluble

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

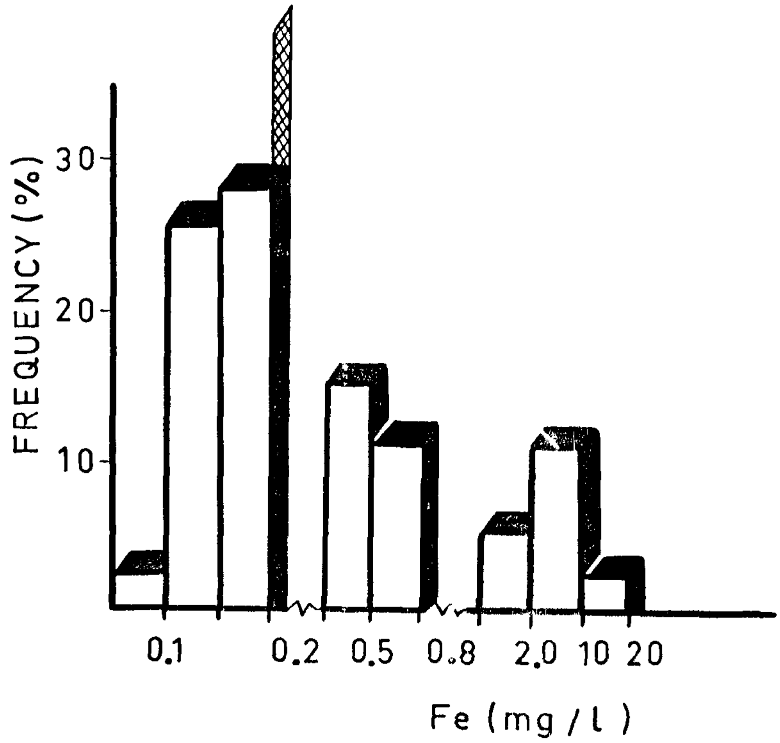
The comparison of iron determined by the two methods employed is statistically compatible with the null hypothesis of there being no difference between the mean of the results for the AAS and phenanthroline methods (Table I). Fisher's "t" for the 14 degrees of freedom and a 95 % confidence level is 2,145 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*.

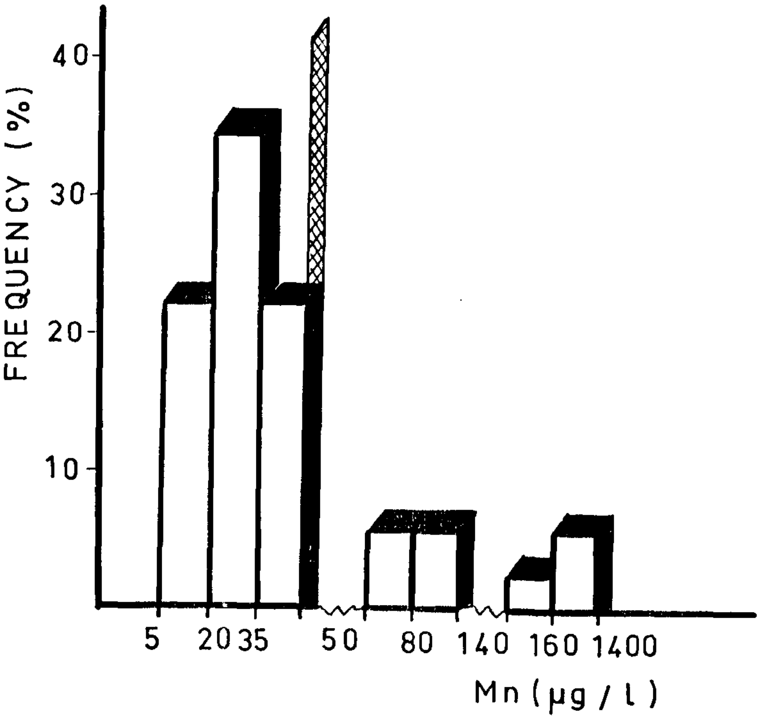
The manganese/iron ratio of all samples is in the range 0,05 to 0,27 regarded by Plochniewski (1972) as typical of Jurassic and Cretaceous waters. Two samples of prequaternary origin lie outside this range (Table II).

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-Eleizegui, 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			
1	7	Soft (40–200)	0,10–0,17	8,6–38,7	0,05–0,27
10	15–30	Very soft (200–500)	0,08–1,70	16,8–63,3	0,01–0,22
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	6×10^2–14×10^2	–

(*) Hardness expressed as mg/*l* of $CaCO_3$
(**) 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	mg/litre 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 (Plochniewski 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
Aquifers 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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