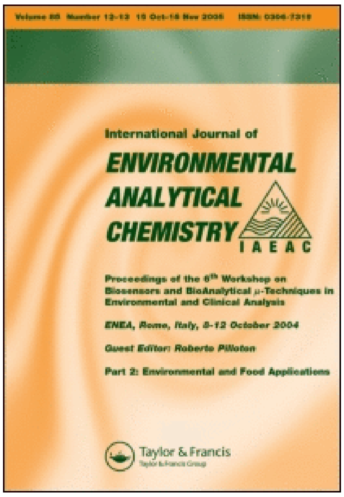

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Iron Determination in the Environment by Solvent Extraction and Atomic Absorption Spectrophotometry

F. Salinas[a]; J. G. March[b]
[a] Department of Analytical Chemistry, Faculty of Sciences, University of Extremadura, Badajoz, Spain
[b] Department of Analytical Chemistry, Faculty of Sciences, University of Palma de Mallorca, Spain

To cite this Article Salinas, F. and March, J. G.(1984) 'Iron Determination in the Environment by Solvent Extraction and Atomic Absorption Spectrophotometry', International Journal of Environmental Analytical Chemistry, 18: 3, 209 — 214
To link to this Article: DOI: 10.1080/03067318408077002
URL: http://dx.doi.org/10.1080/03067318408077002

Intern. J. Environ. Anal. Chem., 1984, Vol. 18, pp. 209–214
0306-7319/84/1803-0209 $18.50/0

Printed in Great Britain

Iron Determination in the Environment by Solvent Extraction and Atomic Absorption Spectrophotometry

F. SALINAS

Department of Analytical Chemistry, Faculty of Sciences, University of Extremadura, Badajoz, Spain

J. G. MARCH

Department of Analytical Chemistry, Faculty of Sciences, University of Palma de Mallorca, Spain

(*Received February 2, 1984; in final form April 20, 1984*)

A simple, sensitive and selective method by solvent extraction and atomic absorption spectrophotometry for the determination of iron is described. The method is based on the extraction of the ion-pair formed between benzohydroxamic acid-iron(III) complex and trioctylmethylammonium cation (Adogen 464) in methylisobutyl ketone. The iron quantities are estimated in water, soil and plant samples.

KEY WORDS: Solvent extraction, atomic absorption spectrophotometry, iron.

INTRODUCTION

Iron is very important in life and development of vegetables. It is an essential element that participates as structural component and as cofactor of some enzymes. The quantity of iron in the leaves of plants (together with the quantity of other inorganic species, such as manganese, zinc, copper, boron and molybdenum) can be taken as an indication of their nutritive state. A periodic analysis allows one to detect deficiencies before appearance of patologic symptoms. On the other hand, the quantity of iron in soils, is interesting for agriculture when selecting the most adequate compost.

The aim of this work is to propose a new method for iron determination in leaves and soils. This method has also been applied to waters.

One of the instrumental techniques of analysis more used is atomic absorption spectrophotometry (a.a.s.) for its sensitivity, selectivity and quickness. The combination of a.a.s. with liquid-liquid extraction is a simple and recommendable method to increase the sensitivity, and reduce the interference from the matrix.[1]

Hydroxamic acids (R—CO—NH—OH) react with Fe(III), forming complexes whose structure was studied.[2] One of these, is benzohydroxamic acid (C_6H_5—CO—NH—OH) that has an easy synthesis and can also be commercially achieved.

In this paper a new method for iron determination by a.a.s. is proposed. The method is based on the formation of anionic complex of iron(III) and benzohydroxamic acid which is extracted as ion-pair using trioctylmethylammonium cation. As organic solvent methylisobutyl ketone has been chosen due to its non-problematic combustion.

EXPERIMENTAL

Apparatus

Perkin–Elmer 703 atomic absorption spectrophotometer equipped with standard burner of 10 cm flame path. The optimum instrumental conditions are summarized below:
wavelength, 248.3 nm; lamp current, 30 mA; Slit width, 0.2 nm; air flow rate, $17.5\,l\,min^{-1}$; acetylene flow rate $1.3\,l\,min^{-1}$; height of lightpath above burner, 1.5 cm; rate aspirate, $4\,ml\,min^{-1}$. Crison 517 pH meter provided with a glass calomel electrode.

Reagents

A standard iron(III) solution was prepared from iron(III) chloride. Its final concentration was determined gravimetrically. Benzohydroxamic acid (BHA) was synthesized by Blatt method.[3] A 0.04 M solution was prepared in water. A 1 M buffer solution of pH 6.1 was prepared from NaH_2PO_4 and NaOH. A 6×10^{-3} M trioctylmethylammonium chloride (Adogen 464) solution was prepared in methylisobutyl ketone (MIBK). All other reagents were of analytical grade.

Procedure for iron(III) determination

Take an aliquot of the sample solution containing 0.3–12 μg of iron into a separatory funnel, add 5 ml of reagent solution and 5 ml of buffer solution ($pH = 6.1$). Dilute to 25 ml with water. Mix well. Add 5 ml of Adogen 464 solution. Shake for 10 min. with a mechanical shaker and allow the phases to separate. Transfer the organic layer into a glass-stoppered tube filtering by a paper moistened in MIBK. Aspirate the organic layer directly into the air-acetylene flame. Measure the atomic absorption at 248.3 nm using MIBK as a blank.

Determination of iron in environmental samples

The determination of iron in water was carried out without previous treatment of the sample and following the procedure with an adequate phase-volume ratio. The determination of iron in soil was carried out from 50–200 mg of sample, dried at 110°C and digested with H_2F_2 and $HC10_4$. The determination of iron in leaves was carried out from 0.1–1 g of sample, dried at 80°C, reduced to ashes in a muffle furnace at 500°C and digested with HCl.

RESULTS AND DISCUSSION

Effect of pH and buffer concentration

The effect of the pH of the aqueous solution on the Fe(III)–BHA complex extraction into MIBK and into MIBK-Adogen 464 solution was studied using a fixed Fe(III), Adogen 464 and BHA concentrations and varying the pH of the aqueous solution. The extraction yields have been calculated by determining iron from both aqueous and organic phases after extraction. The data are summarized in Table I. Better iron extraction yield occurred in presence of Adogen 464 and is higher than 97% for pH values between 5.7 and 6.5. A buffer of $pH = 6.1$ and composition NaH_2PO_4/Na_2HPO_4 was chosen. Influence of the total buffer concentration has been studied using 7.7 μg Fe(III). Total buffer concentration comprised between 0.12 M and 0.30 M do not affect the atomic absorption of

TABLE I
Effect of pH on extraction of 50 μg of iron(III) into MIBK and into MIBK-Adogen 464 solution. $V_{aq} = 25$ ml, $V_{org} = 5$ ml.

pH	%E MIBK-Adogen 464	%E MIBK
3.2	51.0	13.2
4.0	75.3	25.0
4.9	92.3	32.4
5.7	98.9	41.0
6.1	99.3	42.5
6.5	97.7	32.3
7.3	96.5	18.3
8.8	90.0	12.3
10.2	83.2	3.0
12.1	75.1	—

the organic phase (A = 0.150). With inferior concentrations to 0.12 M higher signals are obtained (0.01 M, A = 0.210; 0.02 M, A = 0.200; 0.04 M, A = 0.193; 0.08M, A = 0.165) and higher concentrations to 0.30 M decrease the signal (0.40 M, A = 0.142; 0.80 M, A = 0.050). A total concentration of 0.2 M was chosen.

Effect of BHA and Adogen 464 concentrations

A molar excess of 45 in BHA and 8 in Adogen (or higher) were adequate for the extraction of the amounts of iron used. However, in the method a higher molar excess of the reagents is recommended because the reagents are also consumed by the interfering metal ions, and the presence of an excess of the reagents is essential for the complete complexation and extraction of the iron.

Shaking time and stability

The extraction is complete after shaking for 5 min, however, when the extraction was carried out in the presence of high amounts of foreign ions, higher shaking times for the complete extraction of iron must be employed. The atomic absorption of the extracted ion-pair of the Fe(III)-BHA complex with Adogen 464 in MIBK remains constant for at least 3 weeks if it is stoppered in a closed glass tube.

Effect of phase-volume ratio

The effect of phase-volume ratio was studied with 10 μg Fe(III) and with 5 ml of organic phase and varying the volume of the aqueous phase in the range 10–125 ml, giving a phase-volume ratio ranging from 2 to 25. The atomic absorption remains constant for phase-volume ratios comprised between 2 and 10 ($A = 0.202$). For higher phase-volume ratios, the atomic absorption increases ($V_{aq}/V_{org} = 15$, $A = 0.225$; $V_{aq}/V_{org} = 20$, $A = 0.260$; $V_{aq}/V_{org} = 25$, $A = 0.340$). This increase is fundamentally due to the dissolution of MIBK in the aqueous phase.

Characteristics of the analytical method

Using an aqueous phase of 25 ml and an organic phase of 5 ml, as previously described, was found that the calibration curve was linear up to 0.50 ppm Fe(III). The sensitivity was 0.01 ppm for 1% absorption ($A = 0.0044$). The coefficient of variation was 1.8%, calculated from ten replicated analyses with 0.40 ppm in the aqueous phase (25 ml). The interference of diverse ions was also studied with the same volumes of organic and aqueous phases. Moderate amounts of most of the ions did not interfere with the determination. Tolerance of diverse ions were: 80 ppm or more for Pb(II), Hg(II), Cu(II), Mg(II), Ca(II), Sr(II), Ba(II), Co(II), Cd(II), Ni(II), Zn(II), V(V), Mo(VI), Cl^-, $SO_4^=$, NO_3^-; 40 ppm for Mn(II), Cr(III); and 20 ppm for Al(III), respectively, for the determination of 0.40 ppm of iron.

Determination of iron in environmental samples

The data on the determination of iron in water, plant and soil samples are given in Table II. In all instances, the standard addition method was employed. In order to detect the existence of possible interferences, the iron recovery was calculated by comparing the results obtained before and after the addition of the iron standard solutions. The results showed that the recovery of iron was satisfactory.

TABLE II
Iron determination in environmental samples

Sample	Iron found	% Standard deviation	Recovery (%)
Spring water	0.21 ppm[a]	2.0	98
Underground water	0.02 ppm[a]	19.5	95
Industrial water	0.54 ppm[a]	1.8	97
Industrial water	2.20 ppm[a]	1.8	97
Sea water (Formentera)	0.04 ppm[a]	16.3	95
Sea water (Alcudia. Mallorca)	0.05 ppm[a]	15.2	95
Sea water (Palma de Mallorca)	0.09 ppm[a]	8.3	95
Soils	1.53–0.09%[b, c]	2.8–3.4	96–98
Almond's leaves	0.010%[c]	3.3	96
Vine's leaves	0.008%[c]	3.5	94
Alfalfa	0.024%[c]	2.9	97

[a] Eight separate determinations.
[b] Range for highest and lowest concentrations found.
[c] Three separate determinations.

References

1. M. S. Cresser, *Solvent extraction in flame spectroscopic analysis* (Butterworth and Co. Ltd., London, 1978).
2. L. M. Epstein and M. W. Stranb, **8**, 453 (1969).
3. A. H. Blatt, *Organic Syntheses* (John Wiley and Sons, New York, 1947), Vol. II, 2a ed.