

ORIGINAL PAPER

X. J. Li · P. Schramel · H. Z. Wang · P. Grill
A. Kettrup

Determination of trace metal ions Co, Cu, Mo, Mn, Fe, Ti, V in reference river water and reference seawater samples by inductively coupled plasma emission spectrometry combined with the third phase preconcentration

Received: 28 July 1995 / Revised: 11 October 1995 / Accepted: 20 October 1995

Abstract A combination of DAM-SCN⁻ third phase extraction and inductively coupled plasma emission spectrometry (ICP-AES) is used for the determination of trace metal ions in a river water and a seawater reference material. An implementation of the third phase extraction prior to ICP-AES allows a preconcentration of trace elements (Co, Cu, Mn, Fe, V, Ti, Mn) by a factor ranging from 33 to 45. A complete separation of these elements is accomplished from matrices, normally affecting the excitation characteristics of ICP and suppressing the elemental signals severely. Different factors, including pH of the solutions, amounts of reagents, matrix effects, have been investigated and optimized. Under the conditions selected, the limits of determination have been in the range of 0.02 to 0.6 µg/L. The system has been successfully applied to the determination of Cu, Mn, V in the reference river water SLRS-3 and Mo in the reference seawater NASS-3. The results were in a good agreement with the certified values.

Introduction

Although ICP-AES has been applied as a powerful multi-elemental detection technique for different kinds of samples [1–4], its application to the analysis of highly saline water remains limited. This is attributed to the low tolerance of the technique to some matrix elements existing in saline water, such as Na⁺, Mg²⁺, Ca²⁺ which influence the excitation conditions of the ICP resulting in severe suppressions of the signals. Another restriction is the often

insufficient detection limit, especially for water samples. Thus, preconcentration and or matrix separation are necessary using ICP-AES for the determination of trace elements in this kind of samples.

Liquid-liquid phase extraction is considered to be an effective preconcentration and separation method for trace metal ions. In spite of its wide-spread use, the method of two-phase liquid-liquid extraction for separation and preconcentration of inorganic compounds has some drawbacks. A low enrichment factor is one of them, since in most cases the phase volume ratio (organic solvent: aqueous phase) is in the range from 1:1 to 1:10. At this point, three-phase extraction (the third phase extraction) has proved to be an effective alternative for two-phase extraction. In some two-phase liquid-liquid extraction systems a third phase is formed which is not soluble neither in the aqueous phase nor in the organic phase. It is called the third phase or microphase owing to its small volume. In this third phase normally an enrichment factor from 10 to 100 can be reached due to the small volume of the third phase (down to 1 ml or less) resulting in high phase-volume ratios up to 100 or more.

The possibility of extraction of trace metal ions from hydrochloric acid medium by using a DAM (diantipyril-methane) third phase system was initiated in 1963 by V.P. Gevopescev et al. [5]. From that time, this system has attracted much attention. B.I. Petrov applied a DAM-oxlaric system to preconcentrate Sn [6] and T.M. Moroshkina used the DAM-SCN⁻ system for the preconcentration and matrix separation of Co, Zr, Ta, Hf, Nb from a steel matrix [7]. The DAM-SCN⁻ system was also utilized by D.K. Zhang to analyze Co in a nickle-base alloy [8].

A third phase extraction system will be formed using the DAM-CHCl₃ extraction system with a mixture of chloroform and an inert diluent such as kerosene or an aromatic hydrocarbon as solvent, provided that DAM is present together with hydrochloric acid and some other anions, e.g. SCN⁻ or I⁻. For the DAM-A⁻ third phase extraction system the following mechanism is proposed: in an acid media, protonated DAM(DAM.H)⁺ combine in the organic phase with the negatively charged complex

X. J. Li · H. Z. Wang
Central Iron and Steel Research Institute, Chemistry Department,
No. 76 Xueyuan Nanlu, Haidian District,
Beijing 100081, P.R. China

P. Schramel (✉) · P. Grill · A. Kettrup
GSF-Forschungszentrum für Umwelt und Gesundheit GmbH,
Institut für Ökologische Chemie, Neuherberg,
D-85758 Oberschleißheim, Germany

ions $(Mam)^-$ of the aqueous phase and produce the ionic associates $(DAM.H)^+(MA_m)^-$ which are the major components of the third phase. The special structure of these ion-pairs which comprise both a hydrophobic and a hydrophilic group make it insoluble as well in the aqueous as in the organic phase and forms therefore the so-called third phase.

Despite its strong ability for concentration and separation, this third phase is rarely used as a pretreatment method for modern instrumental analysis, particularly ICP-AES or ICP-MS. This is due to the complicated structure of the third phase being insoluble in the aqueous and in the organic phase, which cannot be introduced directly into the ICP torch due to clogging and cooling effects. In this work these difficulties were overcome by small volume stripping (2–3 ml stripping reagent). In acidic media, DAM, SCN^- and Co, Cu, Mo, Mn, Fe, Ti, V ions form the third phase complexes. These complexes can be decomposed by alkaline media and the metal ions would be released back to aqueous phases which are introducible for the ICP. This procedure makes the use of the third phase extraction as preconcentration and separation method for ICP-AES feasible.

In this paper, the third phase extraction was for the first time combined to ICP-AES for the determination of trace elements in river water and seawater matrices. The DAM- SCN^- third phase system was found to eliminate completely the suppression effect of saline matrices on the signal intensities of ICP-AES and enrich trace metal ions by approximately 40-fold. The combination of the third phase extraction and ICP-AES was realized by TMAH (tetramethylammonium hydroxide) stripping. The accuracy, precision and feasibility of the system were demonstrated by determining certified trace elements in reference river water SLRS-3 and reference seawater NASS-3. Results obtained were in a good agreement with the certified values.

Experimental

Apparatus. An ICP-AES system, JOBIN-YVON Model 70P ICP-spectrometer, was operated under the conditions listed in Table 1. The sample was introduced with a GILSON autosampler. All elements were measured in simultaneous mode. For pipetting solutions, electric pipettes (RAININ, USA) of changeable volume (0–1000 μ l, 0–10 ml) were used. All glass-ware and other containers were cleaned first by soaking in 5% Mucosal detergent solution and then by 5% HNO_3 , followed by rinsing with ultrapure water.

Reagents. Ultrapure water (Milli-Q, Millipore Germany) was used for all solutions and dilutions. All chemicals were at least analytical grade. 10 mg/L, 200 μ g/L multielemental solutions were prepared by diluting the 1000 mg/L stock standard solution (SPEX) with ultrapure water. 25% tetramethylammonium hydroxide (TMAH) stock solution (Tama Chemicals, Japan) was used for the preparation of 5% TMAH solution. The concentrations of sodium chloride, magnesium nitrate and calcium chloride in artificial seawater were 3.5 g NaCl, 0.5 g $Mg(NO_3)_2 \cdot 6H_2O$ and 0.1 g $CaCl_2 \cdot 2H_2O$ in 100 ml water. The reference river water SLRS-3 and reference seawater sample NASS-3 were purchased from National Research Council Canada.

Table 1 ICP-AES operating parameters

Rf output power		1.2 W
Frequency		40.68 MHz
Argon flow rate,	coolant	15 l/min
	carrier	0.8 l/min
	sheath	0.1 l/min
Integration time		5 s
Wavelength	Co	237.862 nm
	Cu	324.754 nm
	Mo	202.030 nm
	Mn	257.610 nm
	Fe	259.940 nm
	Ti	334.941 nm
	V	310.230 nm

Experimental procedures. In order to produce the third phase, a certain aliquot of the sample (metal ions), NH_4SCN and HCl were placed into a 250 ml separating funnel diluted with ultrapure water up to a total aqueous volume of 200 ml (marked on the separating funnel). Then 5 ml of 0.2 mol/L DAM chloroform-benzene solution (chloroform : benzene = 1 : 1 v/v) was added and extracted for 5 min. After standing for 5 min, the third phase (1 ml) was separated carefully into another separating funnel containing 3 ml chloroform.

The decomposition of the third phase was performed by stripping. Briefly, 3 ml of 5% TMAH solution was added exactly into the third phase obtained from the above described procedure and extracted for 1 min. The aqueous phase was separated, for the subsequent determination by ICP-AES. The operating conditions of ICP-AES are summarized in Table 1. The calibration solutions were treated in the same way as the samples, i.e. they were measured after the third phase extraction.

Results and discussion

Optimization of extraction parameters

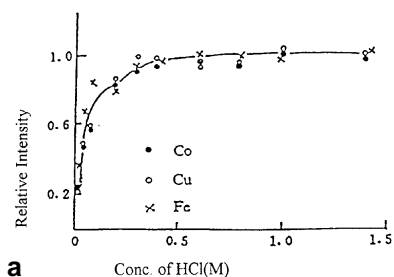
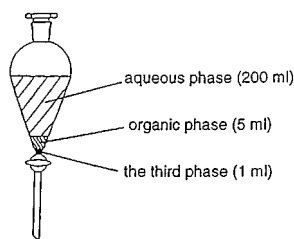
Under appropriate acidity and complexant concentrations, the third phase is produced. Figure 1 illustrates the DAM- SCN^- third phase extraction system. The composition of the three phases are:

HCl, NH_4^+ and SCN^- in the aqueous phase
 $CHCl_3$ and C_6H_6 in the organic phase
 $(DAM.H)^+(MSCN_m)^-$ ion pairs in the third phase

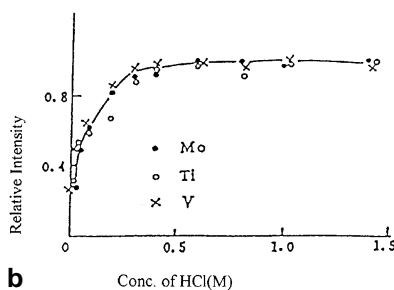
The extraction of Co, Cu, Mo, Mn, Fe, Ti, V with the third phase is carried out by the formation of ionic associates- $(DAM.H) \cdot (MSCN_m)$ between the negatively charged Co, Cu, Mo, Mn, Fe, Ti, V species ($MSCN_m$) and the positively charged counter ions of organic extractant $(DAM \cdot H)$. To optimize this DAM- SCN^- third phase preconcentration system, the influence of concentrations of SCN^- and HCl on the signal intensities of Cu, Co, Fe, Mo, V, Ti were examined. The results were shown by Fig. 2 and 3.

Figure 2 a, b show the pH-dependence of the extraction of the elements. The acidity of the system varied between 0.02 mol/L and 1.4 mol/L HCl. For all elements measured, the intensities increased with increasing acidity up to 0.6 mol/L HCl, then staying constant. An acidity of 0.8 mol/L HCl was chosen for further work. For almost all elements determined, the effect of the SCN^- concentration

Fig. 1 Illustration of the DAM-SCN⁻ third phase extraction

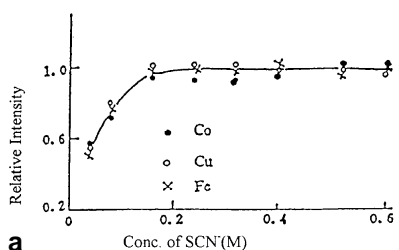


a

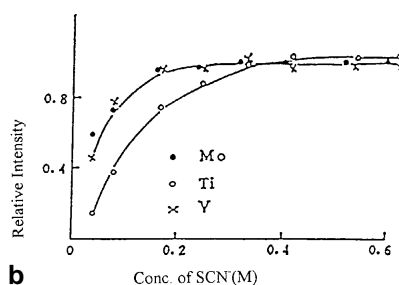


b

Fig. 2 a, b Effect of acidity on the relative intensities of **a** Co, Cu, Fe (200 µg/L), **b** Mo, Ti, V (200 µg/L)



a



b

Fig. 3 a, b Effect of the concentration of SCN⁻ on the relative intensities of **a** Co, Cu, Fe (200 µg/L), **b** Mo, Ti, V (200 µg/L)

was similar (Fig. 3 a, b). The intensities for Cu, Co, Mo, V, Fe were increased with an increasing concentration of SCN⁻ from 0.04 mol/L to 0.16 mol/L. For higher concentrations, the intensities are again constant. Ti was the ex-

ception here. Its intensity increased up to a concentration of SCN⁻ of 0.32 mol/L. For the experiments, 0.4 mol/L of SCN⁻ was selected. It was also found in the experiments that no third phase could be formed when, either the acidity was lower than 0.02 mol/L HCl or the concentration of SCN⁻ was below 0.04 mol/L.

The concentration of DAM chosen for the system was 5 ml of 0.2 mol/L DAM chloroform/benzene (1 : 1 v/v) solution. Higher concentrations would increase the extractability slightly, but the volume of the third phase would also be increased resulting in the need of more stripping reagent. As this would decrease the phase-volume ratio of the original aqueous phase and the stripping aqueous phase the final extraction efficiency of the extraction-stripping system would decrease.

Three ml of 5% TMAH solution was sufficient for saturation stripping.

Analytical features of the system

In order to estimate the analytical features of the combined system of DAM-SCN⁻ third phase extraction and ICP-AES, enrichment factors, detection limits and precisions were examined (Table 2). The enrichment factors for Ti, V, Cu, Mn, Mo, Co, and Fe obtained demonstrate that almost all elements examined could be enriched by the DAM-SCN⁻ third phase extraction/stripping system efficiently. The extraction of Mn with an enrichment factor of only 6 seems not to be sufficient. In spite of this, Mn also could be extracted reproducibly with a precision of 7.4%.

The detection limits were calculated for the concentrations of analytes corresponding to twice the standard deviations of the background intensities. (Although somewhat more reliable estimates of analytical performance would be obtained from limits of determination determined on a 3 σ basis, the 2 σ approach was used here in order to facilitate comparison with previously published data.) In Table 2, the limits of determination for Co, V, Cu, Mo, Fe, Ti, Mn of ICP-AES subsequent to the third phase extraction are listed and compared with detection limits which were obtained by conventional ICP-AES without any pretreatment.

Except for Fe and Mn, all other elements investigated show an adequate improvement in the detection limits. For Cu, Ti and V the detection limits were improved by 20 times or more compared to the determination without preconcentration. The result for Mn was not as good probably due to its lower extractability. The high background in blank for Fe might result in an insufficient improvement in its detection limit, even though the enrichment factor for Fe was high enough. Under simultaneous mode, the measurement capability of ICP-AES for Mo and Co was not ideal. The detection limits for these two elements can be further improved by using the sequential mode.

The precision of the method was examined by using 10 µg/L multielemental solution (Table 3). The precisions obtained were in the range of $\pm 5\%$ (Mn 7.4%, Ti 6.0%).

Table 2 Detection limits (2 σ) and precision

Element	Detection limit after third phase extraction ($\mu\text{g/L}$)	Enrichment factor	Detection limit without third phase extraction ($\mu\text{g/L}$)	Precision ^a %
Ti	0.02	39	0.4	6.0
V	0.03	45	0.8	2.4
Cu	0.04	41	0.9	2.6
Mn	0.08	7	0.2	7.4
Mo	0.2	45	1.3	3.1
Co	0.2	37	2.0	2.1
Fe	0.6	33	1.0	3.7

^aPrecision was estimated at the 10 $\mu\text{g/L}$ level

Table 3 Elimination of the suppression of Na^+ , Mg^{2+} , Ca^{2+} on the relative intensities of ICP-AES signals by the third phase extraction

Element	NaCl (g/L)					
	0	10	20	30	40	50
Co	100	101	104	94	100	92
Cu	100	102	106	97	104	94
Fe	100	100	105	97	99	90
Mo	100	100	106	96	102	93
Ti	100	102	104	95	102	94
V	100	103	105	95	99	92

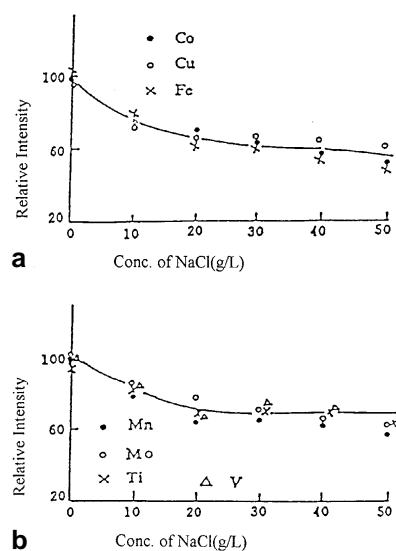
Element	$\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$ (g/L)				
	0	2	4	8	10
Co	100	105	99	106	105
Cu	100	106	100	104	97
Fe	100	109	94	111	105
Mo	100	98	98	97	99
Ti	100	98	112	98	92
V	100	104	98	104	98

Element	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (g/L)				
	0	2	4	8	10
Co	100	99	96	100	102
Cu	100	98	101	94	100
Fe	100	103	100	103	106
Mo	100	91	95	94	97
Ti	100	103	101	96	95
V	100	95	98	94	100

Isolation from high salt-containing matrices

Some macroconstituents existing in water samples, especially in seawater, such as Na^+ , Mg^{2+} , and Ca^{2+} can affect the excitation characteristic of ICP and suppress the signal response severely. The relative intensities of ICP-AES obtained by direct aspiration for Co, Cu, Fe, Mo, Mn, V, Ti in the presence of Na^+ with concentrations ranging from 0 to 50 g/L are shown in Fig. 4.

It can be observed that 50 g/L NaCl in the sample solution could reduce the signal response by about 40%. The third phase extraction can be applied to remove these macroconstituent elements and eliminate their suppression effect. The elimination efficiency of the third phase extraction was investigated by comparing signal intensi-

**Fig. 4a, b** Suppression of Na^+ on ICP-AES signals of **a** Co, Cu, Fe (200 $\mu\text{g/L}$) **b** Mo, Mn, Ti, V (200 $\mu\text{g/L}$)

ties of elements in solutions without Na^+ , Mg^{2+} , Ca^{2+} with those of elements in solutions which contained certain amounts of Na^+ , Mg^{2+} and Ca^{2+} (Table 3). The results indicate that after the third phase separation no significant signal suppression was observed. This proves that the third phase extraction can be employed not only to enrich the trace elements but also to completely separate them from saline matrices.

Recoveries of the method

The recoveries of the proposed procedure were examined by using a tap water and an artificial seawater samples spiked with 2 $\mu\text{g/L}$ of the elements. All elements investigated here could be completely recovered from these two matrices (Table 4).

Table 4 Recovery

Element	Co	Cu	Mo	Mn	Fe	Ti	V
Tap-water	101%	105%	106%	95%	97%	99%	95%
Seawater	100%	98%	102%	95%	115%	105%	99%

Table 5 Values obtained for reference river water and reference seawater

Sample <i>n</i> = 4	Element	Measured ($\mu\text{g/L}$)	Certified ($\mu\text{g/L}$)
SLRS-3	V	0.28 ± 0.01	0.30 ± 0.02
	Mn	3.6 ± 0.1	3.9 ± 0.3
	Cu	1.46 ± 0.04	1.35 ± 0.07
NASS-3	Mo	11.0 ± 0.2	11.5 ± 1.9

Accuracy of the system

The accuracy of the proposed method was validated by its application to certified trace elements in the reference river water sample SLRS-3 and the reference sea water sample NASS-3 (Table 5). For SLRS-3, the elements Cu, V, Mn were measured. In NASS-3 solution, Mo was detected successfully. Other elements in these two reference samples are either uncertified or beyond the detection ability of the presented method. The results were in a very good agreement with the certified values.

Conclusion

Cu, Co, Mo, Mn, Fe, Ti, V at the ng/L to the $\mu\text{g/L}$ concentration level could be determined by ICP-AES simultaneously after a DAM- SCN^- third phase preconcentration. The suppression of ICP-AES signals caused by

saline matrices could be eliminated completely. A more than 30-fold preconcentration was achieved. The precision of the method was lower than 10% at the $10 \mu\text{g/L}$ concentration level. The accuracy of the presented approach was proven by determining certified elements in the reference river water SLRS-3 and the reference seawater NASS-3. Results obtained were in a very good agreement with certified values. The combination suggested provides a simple, rapid, accurate, precise and reliable technique for ICP-AES determination of trace metal ions, especially in the presence of relatively high amounts of salts. The capability of this relatively new (for this type of application) and simply to use extraction technique, which complements the wide field of well known preconcentration and/or matrix separation techniques could be demonstrated. It expands the application of ICP-AES, especially for water samples.

References

1. Que Hee SS, Boyle JR (1988) *Anal Chem* 60:1033–1042
2. Zachmann DW (1988) *Anal Chem* 60:420–427
3. Hartenstein SD, et al (1985) *Anal Chem* 57:21–25
4. Vozzella PA, Condit DA (1988) *Anal Chem* 60:2497–2500
5. Gevopescev VP, Ponosov UN, Selezneva EA (1963) *Zh Analit Khim* 18:1432–1435
6. Petrov BI, Mievena VS, Mahnev NE (1976) *Zh Analit Khim* 31:2142–2146
7. Moroshkina TM, Serbina AM, Petrova GA, Sadkovskay I I (1979) *Zh Analit Khim* 34:872–875
8. Zhang DK (1982) *Fen Xi Hua Xue* 11:430–432