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Journal of Chromatography A, 779 (1997) 139–146

JOURNAL OF CHROMATOGRAPHY A

# Simultaneous determination of toxic arsenic and chromium species in water samples by ion chromatography–inductively coupled plasma mass spectrometry

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Received 6 February 1997; revised 9 April 1997; accepted 15 April 1997

**Abstract**

A method based on ion chromatography in conjunction with inductively coupled plasma mass spectrometry is presented for simultaneous determination of toxic chromium and arsenic species: Cr(VI), As(III) and As(V) using $KNO_3$ at pH 9.8 as eluent. Cr(III), dimethylarsinate, monomethylarsonate, arsenobetaine and arsenocholine did not interfere with the analysis, since Cr(III) was eliminated before analysis and As species were separated from the analytes. The advantages and disadvantages of gradient and isocratic elution in trace speciation analysis by ion chromatography are discussed. With the method described, Cr(VI), As(III) and As(V) could be analyzed at a concentration level of 0.5 μg/l. An application of the proposed method is presented for waste water and drinking water analysis. © 1997 Elsevier Science B.V.

*Keywords:* Water analysis; Metal speciation; Environmental analysis; Arsenic; Chromium; Metals

## 1. Introduction

The toxicological and biological importance of many metals greatly depends upon their chemical form, and therefore the determination of the total concentration of an element is not an appropriate measure for assessing toxicity, environmental impact and the effect of occupational exposure [1–3]. Speciation of arsenic and chromium is important, since they can both appear in forms which are either toxic or non-toxic, or even in forms essential to life. The inorganic forms of arsenic exhibit high toxic levels; As(III) is the most toxic form of water-soluble arsenic species and a suspected human carcinogen, while As(V) is also relatively toxic. The methylated forms, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are less toxic [4–6]. Arsenobetaine (AB) and arsenocholine (AC), for example, are non-toxic [6]. Arsenic compounds have been used for many industrial and agricultural purposes, including pesticides, herbicides and wood preservatives. In biomass, arsenic appears primarily in methylated forms; and the arsenic compounds present in aerated water and soils are usually inorganic [5–7].

Speciation of chromium is of particular interest, since Cr(VI) is very toxic and carcinogenic, while Cr(III) is essential for mammals [8,9]. High chromium concentrations in drinking and groundwater are often of anthropogenic origin. A considerable quantity of chromium can get into soil and from there into surface water also, by means of industrial

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*PII* S0021-9673(97)00402-0

contamination through fertilization and spreading of sewage sludge on arable land. Chromium salts are also used extensively in the metal plating and leather industries and in the manufacture of paints, dyes, explosives and ceramics. In samples collected near industrial plants the concentrations of arsenic and chromium can be quite high. For example, the soil and groundwater near wood preservative plants are often contaminated with both chromium and arsenic, as well as copper.

The benefits of using inductively coupled plasma mass spectrometry (ICP-MS) as a detector in speciation analysis include extremely low detection limits (<0.05 μg/l for most elements), large dynamic range, both multi-element capability and element specificity. These properties are lacking in the UV-absorption and atomic absorption spectrometric (AAS) detectors, for example, which are conventionally used for speciation studies. By combining the separation power of ion chromatography (IC) with ICP-MS, a powerful tool for speciation analysis is achieved. IC–ICP-MS allows the separation and determination of element species with no need for preconcentration. Numerous research groups have applied IC in conjunction with ICP-MS for speciation of either arsenic [10–15] or chromium [16–20]. However, because there is a growing interest in speciation studies, it has become important to find a single method for analysing the toxic species of both arsenic and chromium.

This study presents a method for simultaneous determination of highly toxic arsenic and chromium species As(III), As(V) and Cr(VI) by IC–ICP-MS. Also less toxic DMA and MMA as well as the sum of the non-toxic arsenic species, AB and AC, can be analyzed with the method described. However, in this drinking water study the methylated arsenic species were not of interest, because of their low toxic levels and because no traces of them were found in any samples studied. Applications of the method for drinking and waste water analysis are presented.

## 2. Experimental

### 2.1. Ion chromatography

The pump for ion chromatography was a Pharmacia LKB (Model 2249, Uppsala, Sweden) dual piston reciprocating gradient pump equipped with a Rheodyne-type syringe-loading injector with 0.25 ml loop. All the parts in the pump were of metal-free polyether ether ketone (PEEK) material. The anion column used was a Waters IC-Pak A HC (150×4.6 mm, 10 μm particle size) having trimethyl ammonium functionalized groups on polymethacrylate (Waters Chromatography Division, Millipore, Milford, MA, USA). Also a Waters IC-Pak A (75×4.6 mm, 10 μm) anion column was tested for separation. 20 m*M* $KNO_3$ (analytical-reagent grade grade, Merck, Darmstadt, Germany) adjusted to pH 9.8 with ultra-pure-grade sodium hydroxide (Alfa, MA, USA) was used as a mobile phase at flow-rate of 2 ml/min. The eluent was filtered through a 0.45 μm filter before use.

### 2.2. Inductively coupled plasma mass spectrometry

The ICP-MS instrument was a Fisons Plasma Quad PQ II+ (VG Elemental, Winsford, UK) with a concentric nebulizer, a Scott-type spray chamber and a Fassel-type quartz torch. The ICP-MS operating conditions are presented in Table 1. The peak integration was done manually by measuring the raw counts of the peak heights at *m/z* 52, 53 and 75 using the time resolved programme (TRA) provided by the manufacturer.

### 2.3. Reagents and procedures

Standard aqueous solutions of As(III), As(V), DMA, Cr(III) and Cr(VI) were prepared from arsenic trioxide (Merck), sodium arsenate, cacodylic acid sodium salt (Fluka, Buchs, Switzerland), chromium nitrate and sodium chromate (Merck), respectively.

Table 1
ICP-MS instrumental parameters

| Parameter | Value |
|---|---|
| RF Power, W | 1350 |
| Cool gas flow-rate, l $min^{-1}$ | 13.5 |
| Intermediate gas flow-rate, l $min^{-1}$ | 0.90 |
| Nebulizer gas flow-rate, l $min^{-1}$ | 0.85 |
| Spray chamber temperature, °C | 4 |
| Total acquisition time, s | 500 |
| Time resolved analysis, *m/z* | 52, 53, 75 |
| Dwell time per *m/z*, ms | 300 |

MMA was obtained from Oulu Occupational Health Research Institute, Finland, and both AB and AC from the Pasteur Institute, France. The arsenic and chromium concentrations of the standards were verified by ICP-MS. $HNO_3$ (analytical-reagent grade) used for purification of the ICP-MS and supra pur-grade $HNO_3$ used in gradient elution were obtained from J.T. Baker (Phillipsburg, NJ, USA).

The samples were each passed through a Sep-Pak cartridge (Waters Accell Plus CM, Waters Chromatography Division, Millipore) before injection into the HPLC column.

## 3. Results and discussion

### 3.1. Choice of chromatographic conditions

The use of eluent at a pH higher than 9.2 was necessary, since the $pK_a$ for As(III) is 9.2 [21] and in pH lower than this As(III) was not retained in the anion column, but co-eluted in the void volume with AB and AC. Mobile phases based on carbonate [10,11] and phosphate [15,22,23] solutions have frequently been used for anion exchange of arsenic species. In this study, $KNO_3$ was preferred as eluent, since phosphate buffer has a tendency to erode and clog the nickel sampling cones [24], and carbonate buffer interferes with the analysis of chromium at $m/z$ 52 and 53 causing polyatomic interferences as $ArC^+$ and thus raising the baseline.

At first, gradient elution utilizing increasing $KNO_3$ ionic strength and decreasing pH was used for separating the arsenic species and Cr(VI). The step gradient programme is presented in Table 2. This method gave very good resolution for DMA, As(III), MMA and As(V), as presented in Fig. 1. AB and AC co-eluted in the void volume and thus were separated from other arsenic species. However, the increasing $HNO_3$ concentration in the gradient programme caused high background at $m/z$ 52 and 53 due to dissolution of stainless-steel parts existing in the analytical column. The high baseline increased the Cr(VI) detection limit to 5 μg/l, determined as three times the standard deviation of the baseline, which is too high for drinking water analysis. The detection limits for As(III) and As(V) were 0.5 μg/l. The other disadvantage encountered was the chromium blanks originating from eluent used in re-equilibration step (Table 2) between the analyses. When shorter re-equilibration time was used, the blank decreased, but 20 m*M* NaOH for 15 min and 0.5 m*M* NaOH for 5 min was required to re-equilibrate the system i.e., back to pH 9.7. Since the volume of the eluent used for re-equilibration was about 160 times higher than the volume of the samples injected, even extremely low chromium amounts in the eluent can cause blank problems when concentrating in the column. Cr(III) blank values were especially high, but also some Cr(VI) was observed in the chromatogram.

Because the increase of the baseline and because the chromium blanks could not be eliminated with the gradient conditions used, isocratic conditions were preferred, although these did not give as good resolution for arsenic species, but they did in this case result in shorter analysis times, with no need for re-equilibration, and gave satisfactory separation, nonetheless. Even though DMA and As(III) were not separated to the baseline, their separation was good enough even at a 100 μg/l concentration level, since the peak heights were not affected.

Table 2
The step gradient programme

| Time (min) | 0.05 m*M* NaOH (%) | 40 m*M* $KNO_3$ (%) | 80 m*M* $HNO_3$ (%) |
|---|---|---|---|
| 0 | 98 | 2 | 0 |
| 1 | 95 | 3 | 2 |
| 2 | 87 | 3 | 10 |
| 4 | 65 | 25 | 10 |
| 6 | 60 | 25 | 15 |
| 7 | 0 | 50 | 50 |
| 15 | 0 | 50 | 50 |

The column was a Waters IC-PAK A HC and the eluent flow-rate was 2.0 ml/min.
The column was re-equilibrated for 15 min with 20 m*M* NaOH and for 5 min with 0.05 m*M* NaOH before the next injection.

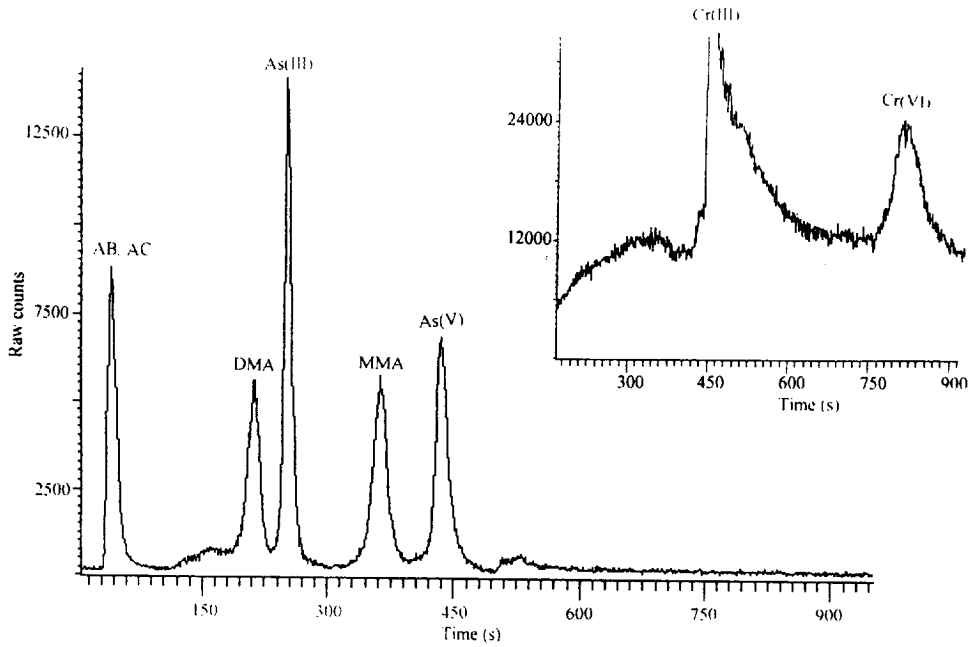


Fig. 1. Chromatogram at $m/z$ 52 and 75 for the separation of 10 μg/l AB, AC, MMA, DMA, As(V) and 20 μg/l of As(III) and Cr(VI) using gradient elution. The gradient programme is presented in Table 2. The Cr(III) was accumulated in the column during the re-equilibration step.

Isocratic ion chromatographic separation of Cr(VI) and arsenic species was performed using 20 m*M* $KNO_3$ at pH 9.8. A typical chromatogram for a standard solution is presented in Fig. 2. No species conversion was observed during analysis; this was tested by studying only one species at time. Also a shorter Waters IC-Pak A (75×4.6 mm, 10 μm) anion column was tested for separation. In this column, DMA and As(III) were not separated under any of the conditions studied, i.e., at pH range 9.3 to 10.5 and $KNO_3$ concentration range 5 to 20 m*M*. Further increasing of the pH dirtied the skimmer cone quickly, decreasing the sensitivity; and lower ionic strength increased significantly the analysis time and detection limits of later eluting As(V) and Cr(VI).

### 3.2. Elimination of cationic species

Eluent at pH 9.8 was needed to separate As species. However, Cr(III) precipitated as $Cr(OH)_3$ in this pH [25] eluting in the baseline and did not cause any peaks in the chromatogram. In order to prevent the disturbances and increase of the baseline signal, Cr(III) was eliminated before analysis by passing the samples through a Sep-Pak cation exchange column. The recoveries for Sep-Pak extraction were studied by measuring the species concentrations before and after extraction using graphite furnace (GF) AAS (Model 1100 B, Perkin-Elmer, Norwalk, CT, USA) or ICP-MS. The recoveries for a well water sample (pH 8.2) spiked with 1 μg/l and 10 μg/l of As(III), As(V), DMA, MMA, AB, AC, Cr(III) and Cr(VI) and for a standard solution of 50 μg/l at pH 3.0 are presented in Table 3. Cationic Cr(III) was totally eliminated during Sep-Pak extraction at pH 3.0 and 8.2, while this procedure did not affect the recoveries for As(III), As(V), DMA, MMA and Cr(VI). AC was totally eliminated at pH 8.2, but not at pH 3.0.

### 3.3. Method characteristics

The detection limits, calculated as three times the standard deviation of the baseline, were 0.5 μg/l for As(III) and As(V), 0.4 μg/l for Cr(VI) at $m/z$ 52

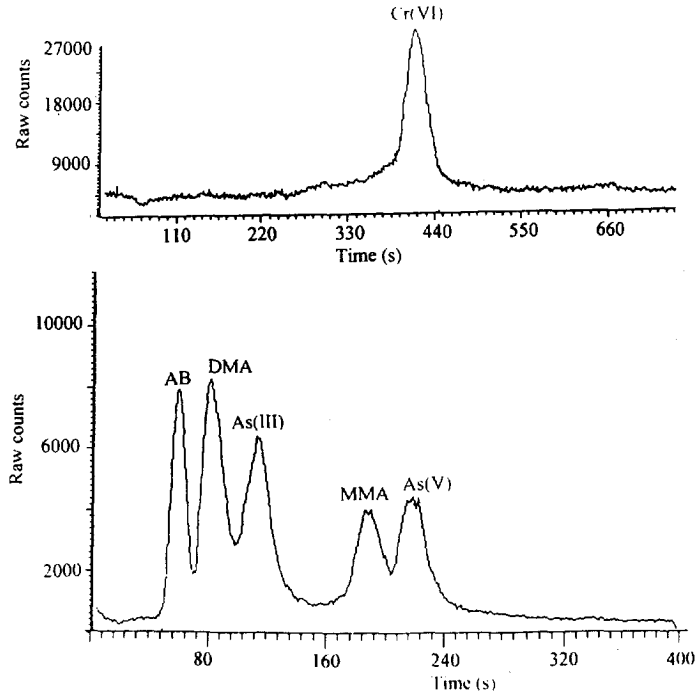


Fig. 2. Chromatogram for the separation of 10 μg/l AB, DMA, As(III) and 6 μg/l MMA and As(V) at $m/z$ 75 and 10 μg/l Cr(VI) at $m/z$ 52 using isocratic conditions with 20 m$M$ $KNO_3$ eluent at pH 9.8. Other conditions as described in Section 2.

and 0.5 μg/l at $m/z$ 53. The relative standard deviations expressing the repeatabilities for the method, were lower than 7% for standard solution containing 4 μg/l As(III) and Cr(VI) and 3 μg/l As(V). The regression coefficients ($R^2$) in the range 1–100 μg/l were 0.999 or better for all the components. The linear calibration data were $y=445x+1300$ for As(III), $y=430x+1148$ for As(V), $y=7400x+1680$ for Cr(VI) at $m/z$ 52 and $y=590x+204$ for Cr(VI) at $m/z$ 53. The recoveries for experiments performed on drinking water samples spiked with 5 μg/l of analytes ($n=5$) were 93–106% for Cr(VI), 93–103% for As(III) and 96–107% for As(V). These recoveries are quite consistent with the repeatabilities of the method, indicating that the drinking water matrix did not interfere with the analysis.

### 3.4. Polyatomic interferences

The large concentrations of chlorine (at $m/z$ 75, $m/z$ 53) and carbon (at $m/z$ 52) can cause polyatomic interferences, if not resolved from the analytes. An $ArC^+$ peak originating from carbonate and some organic compounds (TOC 15 mg/l) appeared

Table 3
Recoveries for arsenic and chromium species after cation exchange Sep-Pak extraction

| Species concentration | As(III) (%) | As(V) (%) | AB (%) | AC (%) | DMA (%) | MMA (%) | Cr(III) (%) | Cr(IV) (%) |
|---|---|---|---|---|---|---|---|---|
| 1 μg/l pH 8.2 | 101 | 114 | 107 | 8 | 101 | 101 | 0 | 100 |
| 10 μg/l pH 8.2 | 98 | 100 | 100 | 4 | 105 | 96 | 4 | 101 |
| 50 μg/l pH 3.0 | 105 | 97 | 98 | 90 | 97 | 100 | 0 | 102 |

Concentrations were determined by GFAAS and/or ICP-MS before and after extraction.

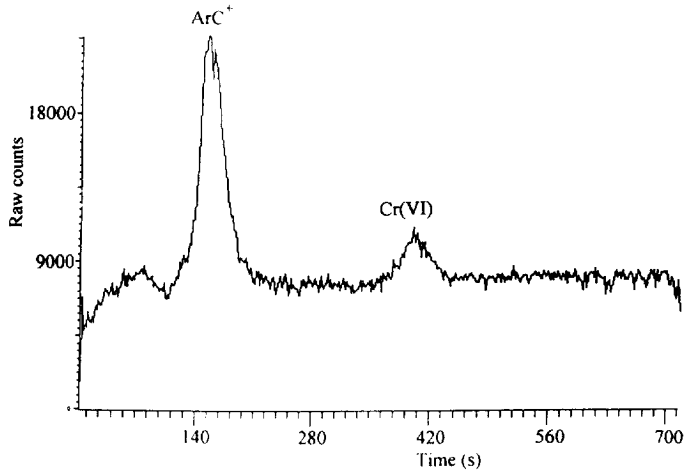


Fig. 3. Chromatogram at $m/z$ 52 for a drinking water sample collected in south-western Finland. The total Cr concentration was 2 μg/l and the Cr(VI) concentration was 1 μg/l. Conditions as described in Section 2.

at about 150 s and thus was resolved from Cr(VI), as presented in Fig. 3. The formation of $ArCl^+$ did not pose a significant problem, since as high chloride concentrations as 1000 mg/l caused only a very small and broad $ArCl^+$ peak at $m/z$ 75, just after As(III). A more significant effect than the polyatomic $ArCl^+$ was the broadening of the As(III) peak with chloride concentration higher than 1000 mg/l. It was advantageous to monitor $m/z$ 53 simultaneously with $m/z$ 75, since in this way the existence of chloride in an unknown sample can more easily be observed as $ClO^+$.

## 4. Applications of the method

The proposed method has been applied for analysis of drinking water and waste water. In Finland, the highest permitted arsenic concentration in drinking water in accordance with the EU drinking water directive, is 10 μg/l and the maximum permitted chromium concentration is 50 μg/l. Only seven drinking water samples containing more than 5 μg/l of total chromium were found in this Finnish study ($n$=40). The highest total chromium concentration was 24 μg/l. Fortunately, only two of the forty samples studied contained any Cr(VI). The Cr(VI) concentrations found in these samples were 1.0 and 0.8 μg/l. The chromatogram presented in Fig. 3 is for a drinking water sample collected in south-western Finland near a cement plant. This sample contained 2 μg/l Cr, of which 1 μg/l was Cr(VI). The method has also been applied for monitoring the Cr(VI) concentrations in waste waters from different industrial plants. The highest Cr(VI) concentration found in an industrial process water from a galvanization plant was 174 mg/l. In most industrial processes applying chromium, Cr(VI) reduced to Cr(III) before the waters are poured into the drain or released to the environment, helps to minimize the environmental drawbacks.

From the forty drinking waters samples studied eight samples contained more than 5 μg/l total arsenic. The highest total As concentration found was 150 μg/l comprising 114 μg/l As(V) and 36 μg/l bound arsenic, and the second highest was 130 μg/l comprising 4 μg/l As(III), 31 μg/l As(V) and 95 μg/l bound arsenic. The chromatogram presented in Fig. 4 is for a drinking water sample collected in western Finland containing 50 μg/l As(III) and 12 μg/l As(V). This As(III) concentration was the highest found in this Finnish drinking water study.

## 5. Conclusions

By using $KNO_3$ at pH 9.8 as eluent for IC–ICP-

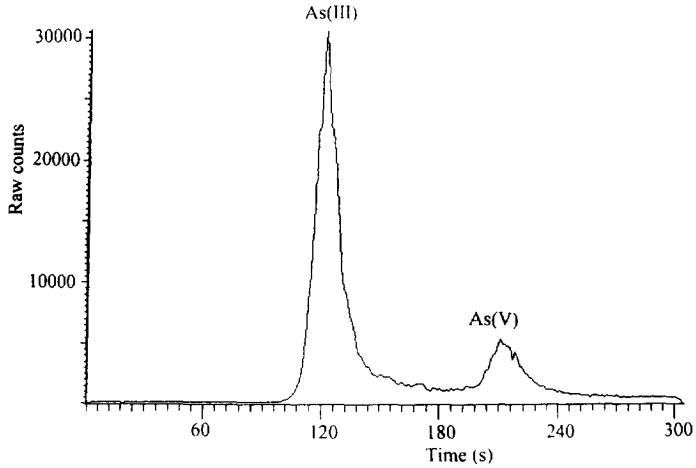


Fig. 4. Chromatogram at $m/z$ 75 for a drinking water sample collected in western Finland containing 50 μg/l As(III) and 12 μg/l As(V). The total As concentration was 81 μg/l. Conditions as described in Section 2.

MS, a simultaneous determination of toxic Cr(VI), As(III) and As(V) was achieved, with detection limits equal to or less than 0.5 μg/l. The proposed method can also be used for analyzing less toxic arsenic species DMA and MMA, and the sum of non-toxic AB and AC, which were not, however, of interest in this study. In drinking water samples collected on different sites in Finland, Cr(VI) was found only at concentrations lower or equal to 1 μg/l, but in industrial waste waters studied higher concentrations of Cr(VI) were found. However, highly toxic As(III) was found in several bore well water samples at quite high (50 μg/l) concentrations.

## Acknowledgments

This work has been supported by the Maj and Tor Nessling Foundation, which is gratefully acknowledged.

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