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Ion-chromatographic screening method for monitoring arsenate and other anionic pollutants in ground waters of Northern Italy

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Abstract

A novel, rapid ion-chromatographic method for screening anionic pollutants in ground water, based on both conductivity and postcolumn spectrophotometric detection, has been developed. A relatively rapid separation of more than ten inorganic and polarizable anions was achieved by coupling an high capacity, hydroxide selective anion-exchange columns (Dionex IonPac AS16) supplied with an electrolytic eluent generator operating in gradient mode. The good control of the selectivity allowed the determination of polarizable anions including arsenate, thiocyanate, thiosulfate and perchlorate without interference from major components present at levels greater than 100 mg l^{-1}. This method was applied to the determination of arsenate in ground water samples collected in industrial and agricultural zones of Lombardia (Northern Italy). No traces of arsenate were detected in any sample, but added arsenate cannot be revealed by chromatographic analyses. This fact can be attributed to different causes, from reduction to the more reduced arsenic form to precipitation or dissolution in organic or inorganic based colloids. Oxidation with hydrogen peroxide seems to be useful for a partial recovery of added arsenate, but a stronger oxidation method, compatible with chromatographic separation, must be studied.

Keywords: Water analysis; Environmental analysis; Arsenate; Inorganic anions

1. Introduction

For many years significant levels of total arsenic (up to 200 μg l^{-1}) have been determined in groundwater of Pianura Padana (Northern Italy) [1,2]. A geochemical source, from leaching of arsenic-rich sedimentary rocks, can explain the high levels of the arsenic compounds in Northern Italian aquifers, but a contribution from anthropogenic activities cannot be ruled out. The presence of arsenic in ground waters represents a significant sanitary problem in this Italian region where most people are supplied with potable water extracted from deep wells. Due to the toxicity of the various arsenic compounds, the World Health Organisation (WHO) suggested a guideline limit for total As of 10 μg l^{-1}, which is more restrictive than the Italian limit of 50 μg l^{-1}.

Chemical speciation of arsenic compounds is a topic under extensive study, because of the diverse toxicity of various arsenic compounds (from the extremely toxic inorganic forms arsenate and arsenite to the harmless arsenobetaine and arsenocholine), the dramatic differences in metabolism of various arsenic species, and the as-yet not well understood roles of arsenic in biological systems [3].

The combination of chromatographic separation

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with element-specific spectrometric detection (such as atomic and mass spectrometry) has proven to be most useful for the speciation of trace levels of arsenic compounds [4–6]. Ion chromatography–mass spectrometry is the most powerful method for the separation and the detection of anionic, neutral and cationic species of arsenic [7], but still it cannot be considered a routine technique. As a consequence, many studies have been devoted to the application of ion chromatography with electrochemical, conductivity and spectrometric detection to the determination of inorganic arsenic compounds in water samples [8–11]. These previous works were limited by interferences from the main ions or by inadequate dynamic ranges or detection limits [11]. These limitations can be overcome by the use of a high capacity column which allows the injection of a relatively large amount of sample (up to hundreds of microliters) and brings the detection limit to the range of low $\mu g\,l^{-1}$. The rapid separation of arsenate, chromate, thiocyanate and perchlorate from major components of ground water was achieved by the optimisation of hydroxide gradient obtained by electrolytic generation [12]. These findings suggest the investigation of the possibility of a rapid ion-chromatographic method for screening anionic pollutants in ground water, based on both conductivity and postcolumn spectrophotometric detection, for simultaneous determination of arsenate and other anionic contaminants, such as chromate. By this screening method, only arsenate has been determined, since in the majority of groundwater samples, arsenic was present as As(V) [6], except for samples that were characterised by a negative redox potential and a pH>7 [3], and/or large amounts of organic matter. The method was applied to a number of Northern Italy ground waters subjected to different sources of contamination.

2. Experimental

2.1. Reagents and standards

1,5-Diphenylcarbohydrazide, sodium acetate, sodium chloride, sodium nitrate, sodium arsenate, potassium dichromate, sodium thiocyanate, sodium selenate, perchloric acid, methanol and sulphuric acid were reagent grade or better (Novachimica, Milan, Italy). Ultrapure water with conductivity $<0.1\ \mu S\,cm^{-1}$ (doubly distilled water) was obtained from a Milli-Q (Millipore, Bedford, MA, USA) deionisation system.

Working standards of different anions were prepared daily by diluting stock standard solutions ($1.000\ g\,l^{-1}$).

2.2. Instrumentation

Chromatographic analyses were performed on a model DX-600 ion chromatograph (Dionex, Sunnyvale, CA, USA) which included one gradient pump GS50, a postcolumn Pneumatic Controller PC10 for postcolumn reagent addition, a ED50 electrochemical detector operating both conductometric and amperometric detection and a AD25 UV–Vis detector operating at 520 nm.

Separations were carried out using a Dionex IonPac AS16 (250×4.0 mm) analytical column and an IonPac AG16 (50×4.0 mm) guard column. Anions were detected by suppressed conductivity detection; suppression was achieved using a Dionex Asrs-Ultra, operated at 300 mA in recycle mode (conductivity detection alone) or external water mode in case of serial conductivity and postcolumn detection.

KOH eluent was electrolytically generated on-line from water using an EG40 eluent generator equipped with EluGen-OH cartridge at a constant flow-rate of $1.0\ ml\,min^{-1}$. The KOH gradient program was composed of four steps: (1) 1.5 m*M* isocratic elution from 0 to 7 min; (2) linear gradient to 10 m*M* from 7 to 15 min; (3) linear gradient to 55 m*M* from 15 to 25 min; (4) 55 m*M* isocratic elution for 5 min.

All measurements were made at room temperature. In all cases, injection of the sample (100 μl) was done at least in triplicate. All the samples were filtered through 0.2-μm filter before injection. Data manipulation and the operation of all the components in the system were controlled by PEAKNET (Dionex) chromatographic software.

2.3. Postcolumn reagent

Chromate was detected after spectrophotometric

postcolumn reaction with diphenylcarbohydrazide based postcolumn reagent: 2.0 m*M* 1,5-diphenylcarbohydrazide, 10% methanol and 0.5 *M* sulphuric acid. The reagent flow-rate was set at 0.5 ml/min. The detector wavelength was 520 nm.

3. Results and discussion

The aim of our analytical separation was to obtain an efficient separation of anions (from acetate to perchlorate) with a wide dynamic range, which makes possible to get a simultaneous quantitative determination of trace and main anionic components. We chose an analytical column (Dionex IonPac AS16) that is a high capacity, anion-exchange column designed for the separation of polarizable anions including iodide, thiocyanate, thiosulfate and perchlorate in a variety of sample matrices. This column was tailored by the manufacturer for use with a hydroxide eluent.

The AS16 column has a capacity of approximately 170 μequiv./column which allows the injection of relatively high amount of sample up to hundreds of microliters, without column overloading, and brought the detection limit in the range of low $\mu g\,l^{-1}$ [12].

The rapid separation of arsenate, chromate and thiocyanate from major components of ground water was achieved by the optimisation of hydroxide gradient obtained by electrolytic generation. The EG40 eluent generator produces high purity potassium hydroxide eluent electrolytically from water, eliminating the need for eluent preparation [13]. The use of carbonate-free hydroxide eluents results in minimal baseline shifts during hydroxide gradients, which provides greater retention time reproducibility, lower background conductivity and lower detection limits for target analytes.

The AS16 column provides excellent separation of a wide variety of other anions as illustrated in Fig. 1. With a potassium hydroxide gradient, ten inorganic anions and polarizable anions are separated in ~30 min. Peak shape and efficiency are greatly improved for the polarizable anions on this column.

Fig. 1a shows that the chromate peak can overlap the phosphate one but it may be interfered with by high levels of sulphate, especially in the case of large volume injection: nevertheless chromate can be easily quantified, in the same analysis, down to $\mu g\,l^{-1}$ levels by using a postcolumn derivatization, after the conductometric detection. Two simultaneous chromatograms are shown in Fig. 1a.

It can be verified in Fig. 1b that arsenate is perfectly resolved from major components, also in a real samples of highly polluted ground water containing more than 100 $mg\,l^{-1}$ of sulphate. The interference from the high level of sulphate limited the maximum injection volume at 100 μl.

The dynamic range was verified by injecting standards of arsenate ranging from 10 to 100 $\mu g\,l^{-1}$ prepared in ultrapure water (Fig. 2a). Excluding the area value of 10 $\mu g\ l^{-1}$ peak, which can be considered the lowest detection limit, a linear calibration curve is generated [y (area)$=2.01x(\mu g\ l^{-1})+15.5$; $R^2=0.9998$] in the range of interest for drinking water samples (25–100 $\mu g\ l^{-1}$). Coefficients of variation of standard replicates ($n=3$) are about 2%. By analysing a standard mixture at 10 $mg\,l^{-1}$ we verify that linearity can be extended up to this level, covering more than three orders of magnitude.

A certified reference material of drinking water (LGC 6010: hard drinking water — metals) has been analysed using this method for arsenate content (Fig. 2b): we determined an arsenate concentration of 56.0 $\mu g\ l^{-1}$, corresponding to an As concentration of 30.2 $\mu g\ l^{-1}$. There is no discrepancy between our result and the certified value of total arsenic (52 $\mu g\ l^{-1}$), since in this sample As(V) compounds are in equilibrium with As(III) compounds as a function of pE and pH values.

Following these promising starting points, we tried to validate the method by adding 100 $\mu g\ l^{-1}$ of arsenate to ground water samples collected in industrial and agricultural zones of Lombardia (Northern Italy).

Unfortunately we observed that arsenate, added at level of 100 $\mu g\ l^{-1}$, disappeared soon after addition to real samples. The stability of inorganic arsenic species in water has been subjected to a number of contradictory studies [14–16]. The disappearance of arsenate was observed in deionised water [17] but no satisfactory explanation has been found for this observation. Arsenate can be reduced to arsenite by biological systems [18] or abiotically by reducing agents such as, for example, Fe(III) and

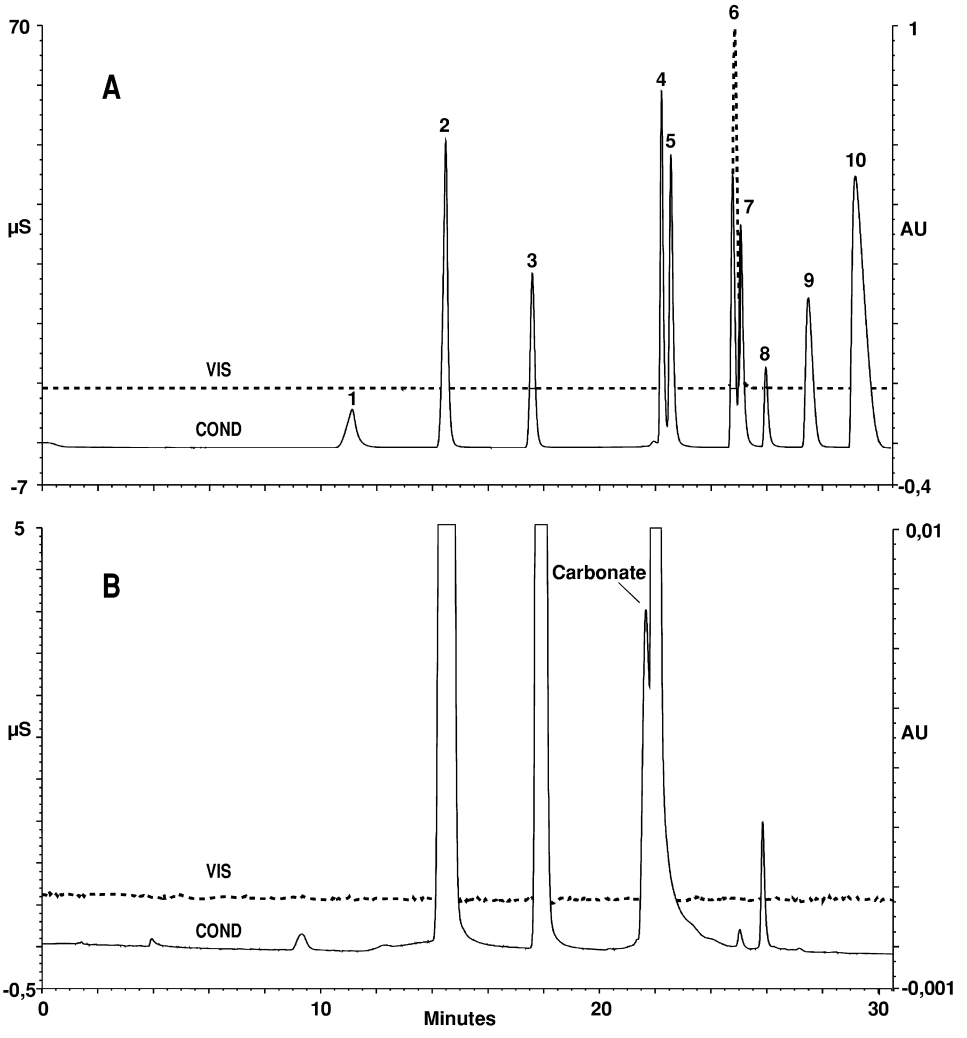

Fig. 1. Gradient separation of common and polarizable anions with both conductometric (COND) and spectrophotometric detection after postcolumn derivatization (VIS). Chromatographic conditions as in the text. (A) Standard solution (B) Ground water sample Rho 6 spiked with 500 $\mu g\,l^{-1}$ of arsenate. Peaks: 1=acetate; 2=chloride; 3=nitrate; 4=sulfate; 5=selenate; 6=chromate; 7=phosphate; 8=arsenate; 9=thiocyanate; 10=perchlorate.

dissolved sulfide [19]. In a ground water matrix, the instability of As(V) compound can be attributed to three different causes

- As(V) compounds was reduced to As(III), due to anoxic conditions in ground water
- The presence of transition metals such as Cu(II), Fe(II) and Fe(III) can cause partial precipitation of arsenic. It was demonstrated that in ground water samples arsenate is partially adsorbed on colloidal ferric oxyhydroxides with a wide range in terms of charge and size [7,20]
- Arsenate can be adsorbed on colloidal organic matter [6] and inorganic arsenic can be methylated by biological activity [3]

The first hypothesis has been discarded because our samples are characterised by E_H ranging from −0.185 to +0.296 V and pH between 7 and 8. Furthermore, we analysed spiked samples by using

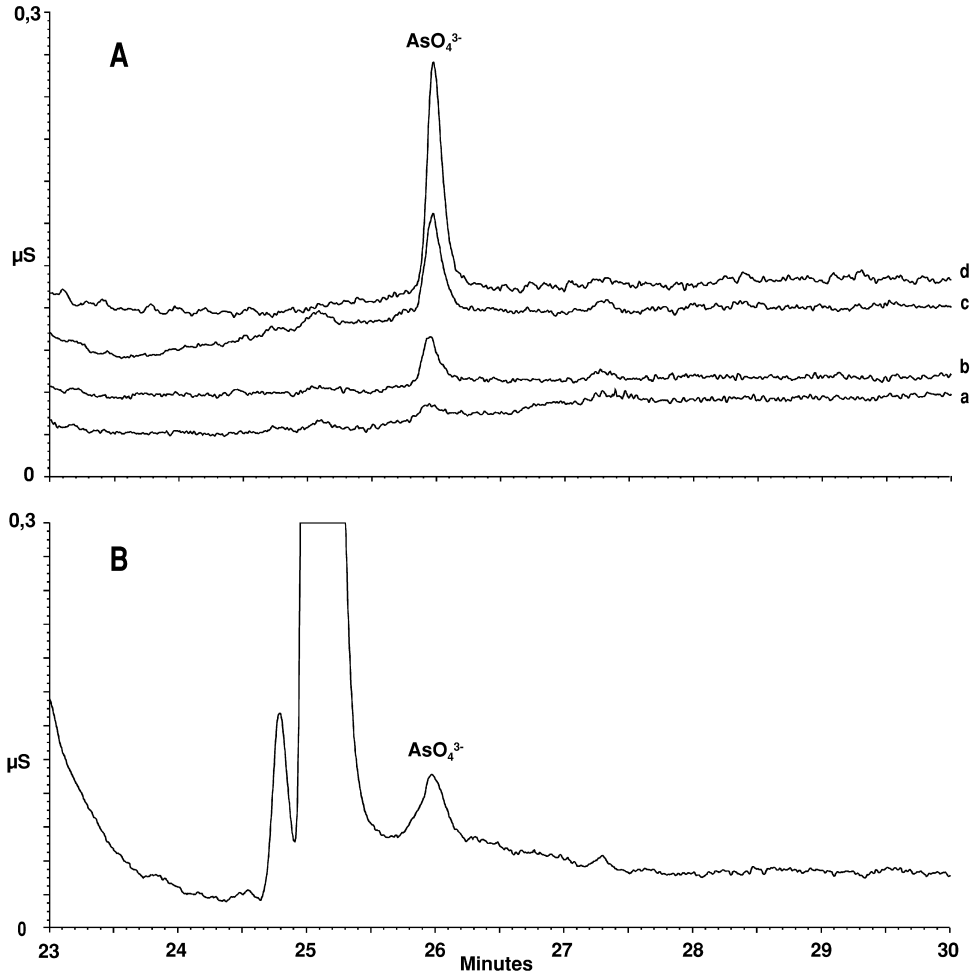

Fig. 2. Comparison of a series of arsenate standards and certified sample. Chromatographic conditions as in the text. (A) Standard, AsO_4^{3-}: a=10 µg l^{-1}; b=25 µg l^{-1}; c=50 µg l^{-1}; d=100 µg l^{-1}; (B) Certified sample LGC 6010: hard drinking water — metals, AsO_4^{3-}: 56 µg l^{-1}.

electrochemical detection (+0.35 V at Pt electrode, as in Ref. [10] in series with conductivity detection, and no As(III) anionic species were detected.

According to Mattusch and Wennrich [7], we acidified samples at pH 2 with hydrochloric acid in order to dissolve metallic oxyhydroxides, but, once again, no arsenate was detected.

The last attempt was to treat samples with hydrogen peroxide, in order to destroy organic matter and to reoxidise arsenic compounds to As(V) [8]. Fig. 3 shows that the use of hydrogen peroxide permitted the detection of traces of arsenate, but the oxidation kinetics are too slow for an affordable analytical method. This experiment suggests that organic matter can be a sink for arsenate in real samples, as reported by Raessler et al. [6], but a stronger oxidation method, compatible with chromatographic separation, has to be found.

4. Conclusions

A relatively rapid separation of more than ten inorganic and polarizable anions was achieved by

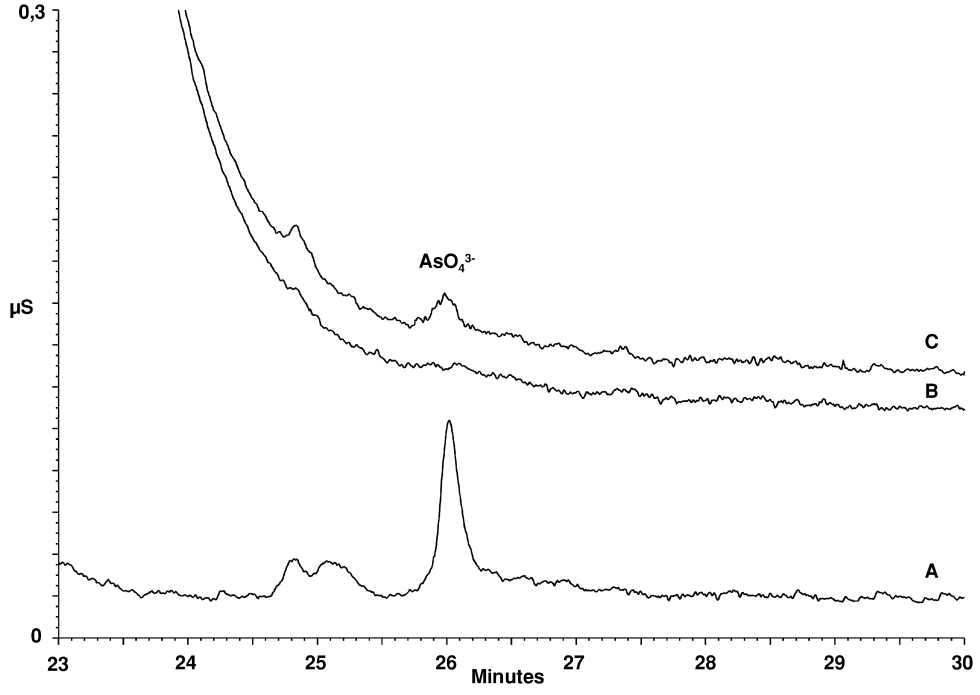

Fig. 3. Effect of hydrogen peroxide on arsenate recovery. Chromatographic conditions as in the text. (A) Arsenate standard AsO_4^{3-}: 100 µg l^{-1}; (B) ground water sample spiked with 100 µg l^{-1} of AsO_4^{3-} and added with hydrogen peroxide, time 0; (C) Sample B, time 1 h.

coupling an high capacity, hydroxide selective anion-exchange columns (Dionex IonPac AS16) supplied with an electrolytic eluent generator operating in gradient mode.

The good control of the selectivity allowed the polarizable anions including arsenate, thiocyanate, thiosulfate, and perchlorate determination without interference from major components present at levels greater than 100 mg l^{-1}. With a moderately large injection volume (100 µl) the simultaneous quantitative determination of trace and major components can be achieved in ground and drinking water. The use of a high capacity latex-based anionic exchanger allowed the injection of high amount of sample (up to hundreds of microliters) and brought the detection limit to the range of low µg l^{-1}.

This method was applied to the determination of arsenate in ground water samples collected in industrial and agricultural zones of Lombardia and a typical chromatogram is shown in Fig. 4. No traces of arsenate were detected in any sample, but neither can the added arsenate be revealed by chromatographic analyses. This fact can be attributed to different causes, from a simple reduction to more reduced arsenic form to precipitation or dissolution in organic or inorganic based colloids.

Oxidation with hydrogen peroxide seems to be useful for a partial recovery of added arsenate, but a stronger oxidation method, compatible with chromatographic separation, must be studied.

The present study suggests that the conductivity detection of low levels of arsenate is strongly dependent on the matrix, sampling and dilution procedures. There is still a strong need for studies devoted to speciation of arsenic compounds, especially in the field of sample collection and preservation, because of rapid equilibrium between organic and inorganic forms of arsenic and complexation reactions.

Future works will be devoted to the validation of

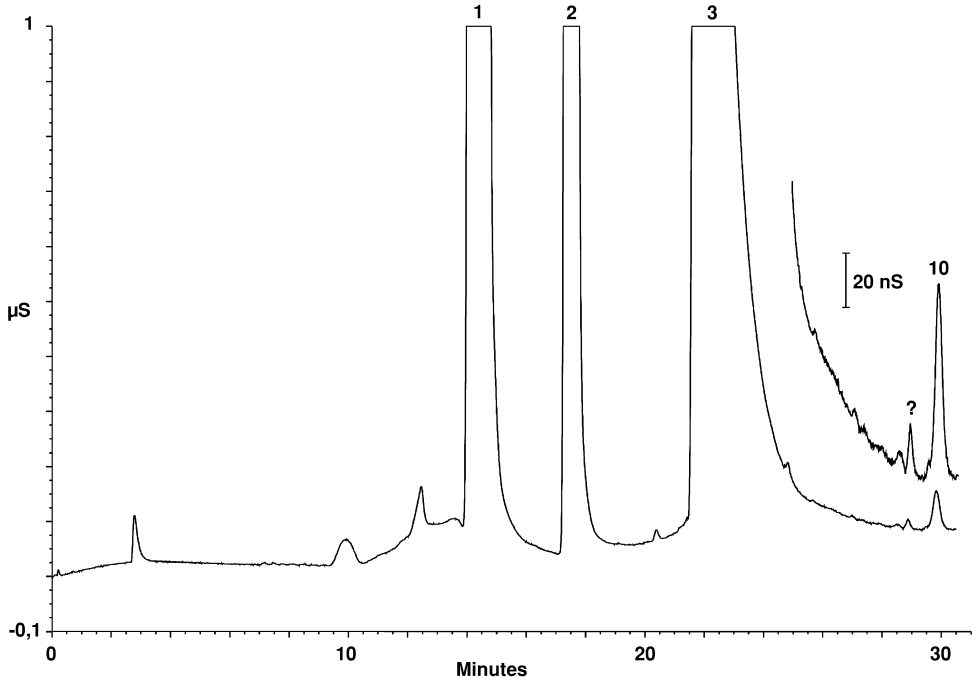

Fig. 4. Typical chromatogram of ground water sample collected in a former industrial zone of Northern Italy. Chromatographic conditions as in the text. The zone of arsenate detection was amplified. Peaks as in Fig. 1a.

similar detection system, and the results, obtained on ground water samples, will be compared with ion-chromatographic–inductively coupled plasma mass spectrometric determinations.

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