

A study of the pollution of the Aries River (Romania) using capillary electrophoresis as analytical technique

F.L. Forray · D.K. Hallbauer

Abstract This paper examines two issues, the extensive pollution occurring in the Aries River, NW Romania, as a result of unchecked discharge of mining effluents into the river system, and the suitability of capillary electrophoresis (CE) as an analytical method for investigations into water chemistry. The results confirm the first objective by providing details on the pollution of the Aries River and its geochemical system and demonstrate the usefulness of CE. In its upper reaches, the river system is characterized by high contents of SO_4^{2-} as a direct result of acid mine effluents and the oxidation of sulphide minerals on mine dumps as well as inflows from settling ponds. Although continuous dilution by natural branch waters and natural water-rock interaction reduces the pollution to some extent, the total level of SO_4^{2-} remains above European averages. The waters of the Aries River, by comparison, contain contents of Cu^{2+} and Zn^{2+} up to 100 times higher than those of unpolluted river water.

Key words Aries River · Capillary electrophoresis · Mining effluent · Romania

Introduction

The famous treasures of gold and silver from the Apuseni Mountains, NW Romania, have been systematically mined since Roman times. After some pause, the mining activity flourished again at the end of the 19th century.

Large amounts of Au, Ag, Cu, Pb and Zn were extracted. Native Tellurium T was first described from this area, as well as several other new minerals.

Apart from the development of the area in the wake of the mining activity, negative effects, such as forest clearing, waste dumps, settling ponds, and installation of technological equipment, had more and more impact on the environment.

Along Ariesului Valley, the main mining centres are Baia de Aries and Rosia Poieni. Other mines located in the Aries hydrographic basin are Masca-Baisoara, Rosia Montana, Bucium and others. They all contribute to the pollution of the river.

The acid mine drainage (ADM), which feeds directly into the Aries valley, represents the main cause of pollution.

Very rarely, are preliminary chemical treatments with calcium hydroxide or lime carried out. Because of its low pH, mine water can carry large amounts of metals (Wieder and Novák 1995; Durkin and Herrmann 1996; Gräber and Frimmel 1996; Robertson 1996) in solution or in suspension.

Another source of pollution is represented by waste dumps and settling ponds, which are usually placed near the Aries River. Because of their position, the waste dumps are purged by rainwater and the resulting water enters the phreatic water and/or the surface water. During periods of heavy rain, the river level rises sufficiently to reach the base of the waste dumps. Thus, large amounts of barren gangue can also be transported into the river system. Further, the stability of the settling ponds can be affected, endangering the downstream areas.

The technology of metal extraction was, in the past, of low efficiency and large quantities of sulphides were left in the host rocks and gangue. The oxidation of these sulphides then led to removal of soluble metal ions from the waste dumps under the effect of rainfall.

In addition to metals, the Aries River also contains organic pollutants, such as flocculants, surfactants, frothers and others, which originate from ore dressing plants. Further pollutants, not connected to mining, and collected by the Aries River, are the result of domestic and agricultural activities. The most important of such substances are nitrates and ammonium.

To study environmental pollution, several analytical methods can be used, which differ mainly in the pre-treatment of samples, detection limits and in the costs of

Received: 1 November 1999 · Accepted: 3 April 2000

F.L. Forray (✉)
Department of Mineralogy, Babes-Bolyai University,
M. Kogalniceanu No. 1, 3400 Cluj-Napoca, Romania
e-mail: forray@bioge.ubbcluj.ro

D.K. Hallbauer
Terra Sounding and Analytical (Pty) Ltd., P.O. Box 2142,
Somerset West, 7129. RSA or Department of Geology,
University of Stellenbosch, Private Bag X1, Matieland 7602,
RSA

the analyses. This paper presents the results obtained by using capillary electrophoresis (CE) for the analysis of water samples. The method was introduced by Hallbauer and others (1995) for the study of groundwater that was in contact with different types of rocks, or for other geochemical analysis (Hallbauer 1994; Hallbauer and others 1997). This relatively new method of analysis combines the advantages of low costs and high accuracy. Until recently, CE was almost exclusively used in the pharmaceutical industry (Jandik and Bonn 1993), but has developed rapidly into an accepted analytical technique for environmental analysis (Dabek-Zlotorzynska and others 1997).

The studied region and its geology

The area under study covers 54 km along the Aries River, between the municipalities of Cheia (downstream) and Muncel (upstream) (Fig. 1). The average flow rate of the river water in this region is about $24 \text{ m}^3/\text{s}$, ranging from $5 \text{ m}^3/\text{s}$ to $63 \text{ m}^3/\text{s}$. On both sides of the valley, the hills rise to between 1000 and 1200 m in height above sea level and the altitude of the river is $\sim 480 \text{ m}$ in the neighbourhood of Baia de Aries (Fig. 2). In the Muncel-Cheia region the flow velocities of tributary brooks into the Aries River varies between 0.01 and $2 \text{ m}^3/\text{s}$.

The studied region is characterized by a very diverse lithology, consisting mainly of metamorphic and sedimentary rocks, but also of intermediary, magmatic rocks of andesitic composition as well as some basic suites (Fig. 1).

The mining activities in the studied region take place in three major areas (Fig. 3).

1. Baisoara area. The mines in the Baisoara area are located along the Iara Valley, on the left tributary of the Aries River, in the neighbourhood of Buru village. The ore-bearing mineral assemblage is usually hosted by



Fig. 2
Photograph of the Aries Valley in the region of study

magnesium-rich skarns, pyroxene skarns and pyrometasomatic bodies. Detailed description of the ore mineralogy and geology are given by Lazar and others (1972) and Stefan and others (1988). The mining activities take place in underground works and the waste material is deposited in waste dumps or in settling ponds on the surface. The leachate waters, downslope of the dumps, are slightly alkaline (pH 8.02) and the amount of transported metals is very low (F.L. Forray unpublished data). The water of the river Iara, which flows into the Aries River in the neighbourhood of Buru village, thus does not contribute significantly to the pollution of the Aries River.

2. Baia de Aries ore. The Baia de Aries area is the main mining field in the study region. Detailed descriptions of the ore mineralogy and geology are given by Lazar (1966), Radulescu and Dimitrescu (1966), Stefan and others (1988), as well as by Udubasa and others (1992a). The mining is at present confined to underground workings. Because of an intensive oxidation of

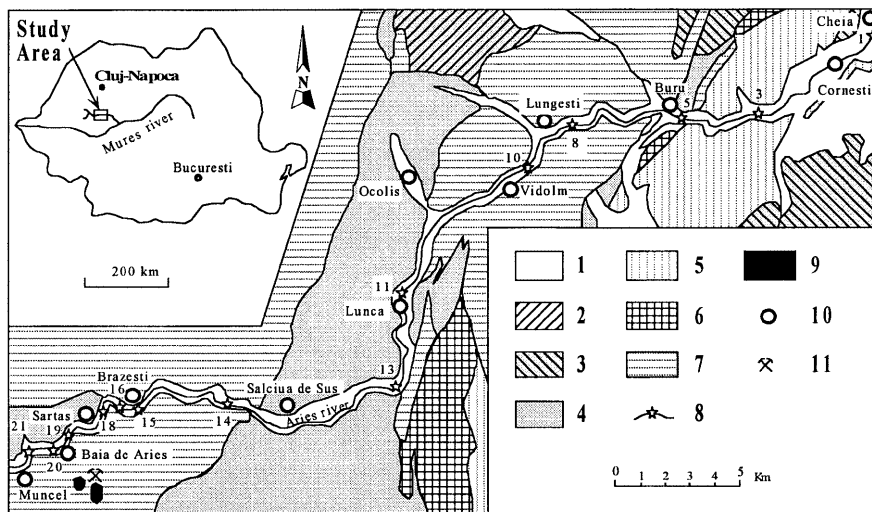


Fig. 1

Simplified geological map of the Aries River valley between the villages of Muncel and Cheia: 1 Quaternary pebbles and sands; 2 Palaeogene continental red clay; 3 Neogene sandstones, clays and sands; 4 Upper Cretaceous sandstone, clays and limestones; 5 Upper Jurassic ophiolites (mainly andesites); 6 Upper Jurassic limestones; 7 Palaeozoic and Precambrian metamorphic rocks (mica-schists with staurolite or garnets); 8 sampling points; 9 andesitic rocks; 10 villages; 11 mines. The flow direction of the Aries River is from west to east (from Muncel to Cheia)

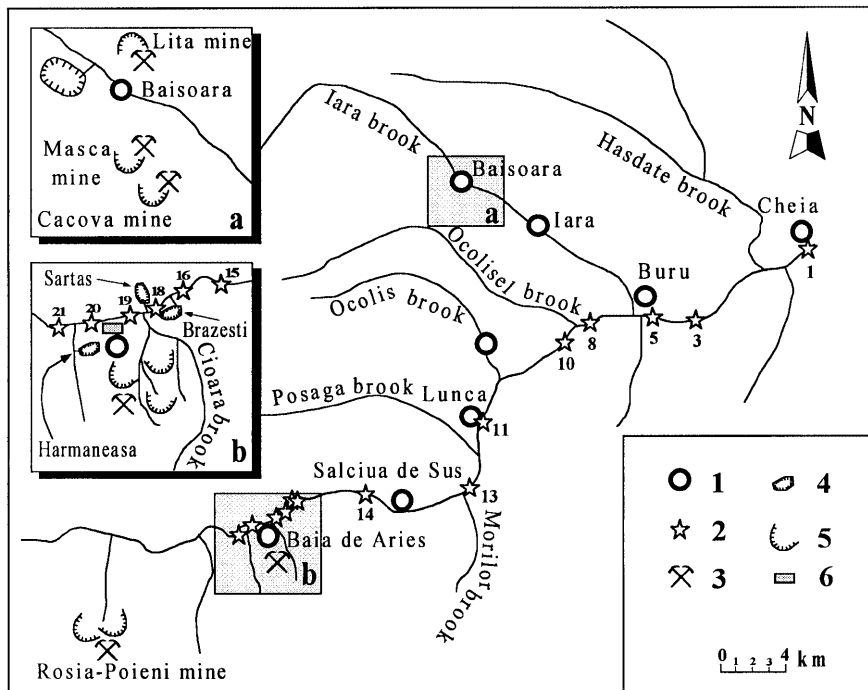


Fig. 3

The main mining regions close to the studied area, which contribute to the pollution of the Aries River: 1 Villages; 2 sampling points; 3 mines; 4 settling ponds; 5 mine waste dumps; 6 crusher/flotation plants

sulphides, both underground and in the waste dumps, the leaching waters are mostly acidic. Their chemistry appears to be directly controlled by the mineralogical characteristics of the ore. In areas where the mineralization is of a hydrothermal-metasomatic type and with limestone as the host-rock, the formation of acidic waters is prevented because of the presence of calcium carbonate. On the other hand, in areas where the veins contain only small amounts of CaCO_3 , and where the host-rocks contain high amounts of pyrite, acidic waters are produced on a large scale. The contents of dissolved metals also increase. The acid mine drainage (ADM) and those components leached from the waste dumps flow directly into the Aries river.

3. Rosia Poieni ore. Rosia Poieni is a porphyry copper-type deposit, with a Cu concentration of 0.4%. Copper ore is being mined in an open pit. Detailed description of the ore mineralogy and geology are given by Ionescu (1974), Ionescu and others (1975), Vlad (1983) and by Udubasa and others (1992b).

Because of the opening of the quarries, considerable amounts of mineralized rock are exposed to rainfall, leaving large amounts of pyrite for intense oxidation and decomposition. This process gives birth to very acidic, leaching waters (pH 2.03) that cannot be buffered because of the very low neutralization capacities of the rocks in the vicinity of Rosia Poieni (F.L. Forray unpublished data). These acidic waters flow into the Aries river lead to a marked increase in pollution.

Methods

Sampling method

The water samples were collected during winter and kept in sterile polyethylene bottles of 100-ml capacity. Each bottle was rinsed several times at the collecting point using river water, in order to reduce the risk of contamination from the manufacture of the bottles. The collecting points were at ~1 m from the riverbank and at a depth of 10 cm. In some areas, especially upstream, it was necessary to break the ice formed at the water surface.

To prevent a subsequent oxidation at the water-air interface, the bottles were completely filled with water and the lid was fixed under water. In the laboratory, in order to preserve the samples, the bottles were kept at 4 °C until measurements were performed. This procedure was recommended by Herr and Gray (1997), and gave good results when the mobility of metals in aqueous solutions was studied. Using these combined techniques of sampling, the preservation of water samples for the study of aqueous species could be assured.

Fourteen water samples were collected between the municipalities of Cheia and Muncel (Fig. 3) along a 54-km stretch of the Aries River. The distance between the collecting points was not constant. When selecting the sampling points, several geological and geomorphological criteria were used. These were changes in geological features within the area and, the water supply from the tributaries or effluents in the mining regions. The causes of specific elemental mobility in aqueous solutions could thus be monitored. The pH values and the conductivity measurements were obtained in the laboratory using a CyberScan CON 20 instrument.

Analytical method (capillary electrophoresis)

High performance liquid chromatography (HPLC) was introduced as an instrumental separation technique in ca. 1970, which was followed by the technique of capillary electrophoresis (CE) about 20 years later. While HPLC is more of an instrumentally controlled analytical technique, CE requires an active input and chemical control by the analyst. From the first marketing of CE instruments, the technique has rapidly developed into a reliable micro-analytical separation technique for a variety of applications (Jandik and Bonn 1993).

The mechanisms responsible for separation in CE are different from those in HPLC. In CE, ionic species are separated based on their charge/size ratios, size being the bulk of the hydrated and/or complexed ionic species. The principle arrangement of a CE separation is shown in Fig. 4. An electrolyte (buffer)-filled fused quartz capillary of $\sim 75 \mu\text{m}$ internal diameter is connected to storage containers of electrolyte. Silanol groups (Si-O-H) are formed on the capillary wall, which have a pK value of ~ 7.7 . H^+ ions form a loose, gliding layer on the wall of the capillary. When an external voltage (5–25 kV) is applied to the electrodes in the containers, a bulk flow or electro-osmotic flow (EOF) of electrolyte (i.e. the electrolyte co-ion) is initiated to the cathode. If a small volume of a sample fluid is injected into the anodic side of the system, the cationic species will move out of the sample plug and separate in the electric field formed, according to their electrophoretic mobilities (μ_c), and also move towards the cathode. Their total migration time, however, is the sum of EOF (or μ_{EOF}) and μ_c . Because only electric forces propel the ionic species, the individual groups form well-defined plugs. Therefore, peaks in CE separations show a lower variance and better resolution in comparison to similar HPLC separations.

At the cathodic side of the capillary the migrating plugs of cations can be detected by their lower absorption in UV light, or indirectly by UV absorption. This requires that the UV absorption of the electrolyte must be about 100 times that of the ionic species in order to arrive at good detection limits.

Sample introduction (Jandik and Bonn 1993) in CE can take two forms: (1) hydrostatic introduction and (2) introduction by electromigration. For hydrostatic introduction or siphoning, the capillary/electrode assemblage is placed in the sample vial, which is then raised for a predetermined time and to a defined level of typically 10 cm above the electrolyte vessel at the receiving end. An introduction time of 30 s then causes a sample volume of $\sim 50 \text{ nl}$ to be injected. For separation, the capillary/electrode assemblage is placed back into the electrolyte vial and a separation voltage (10–25 kV) is applied. In order to achieve a positive flow by hydrostatic introduction a minimum sample volume in the vial of about $300 \mu\text{l}$ is necessary.

Electromigration (EM) is started when the capillary/electrode assemblage is placed into the sample vial and a smaller voltage (1–5 kV) is applied to the electrode. The analyte becomes the terminating electrolyte at the time of introduction. Because of the lower conductivity of the sample only a small amount of fluid is moving into the capillary by EOF. However, the ionic species present in the sample migrate into the capillary under their own electrophoretic mobilities, causing a concentration of ionic species in the sample plug subject to individual mo-

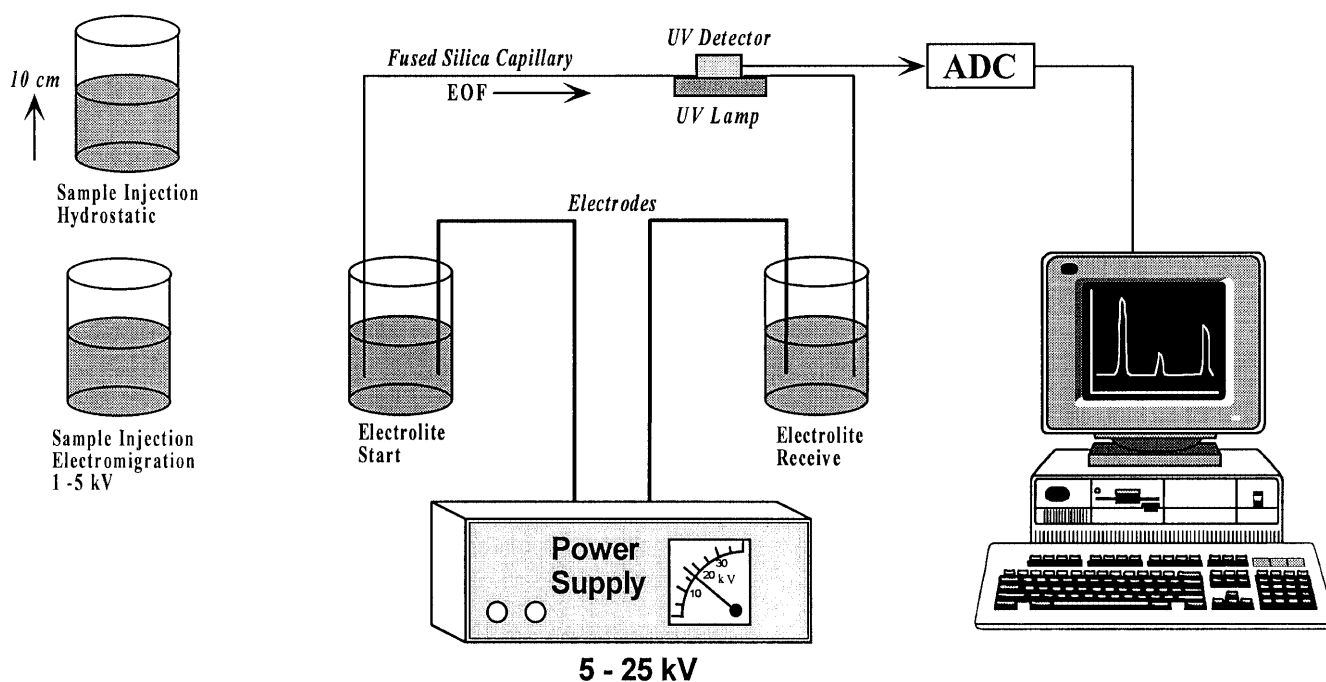


Fig. 4
Principles of CE separation

bilities. The separation is then carried out as described above. Typically, at an electromigration voltage of 4 kV and 10 s introduction time, an enrichment factor of 85 is achieved for potassium. This type of sample introduction is not only different to HPLC techniques, but also allows a lowering of detection limits below the ppb range for some elements such as Li.

One of the requirements for CE is a low conductivity of the sample plug in order to achieve high resolution (Jandik and Bonn 1993). A comfortable detection range for hydrostatic introduction is 0.1–20 ppm for most ionic species. Most cationic species have detection limits for introduction by electromigration introduction of about 0.5–5 ppb. The technique of CE is relatively independent of matrix effects, but a matching of mobilities for the components of the analyte ions and the co-ion is important (Jandik and Bonn 1993; Boden and Bächmann 1996). While the naturally formed silanol groups and the resulting EOF is utilized for the separation of cations, a reversal of the EOF is required for the separation of anions. This can be achieved by adding an osmotic flow modifier (OFM) to the selected co-ion electrolyte (Jandik and Bonn 1993; Dabek-Zlotorzynska and Dlouhy 1994). Such modifiers can be alkyl ammonium compounds or similar,

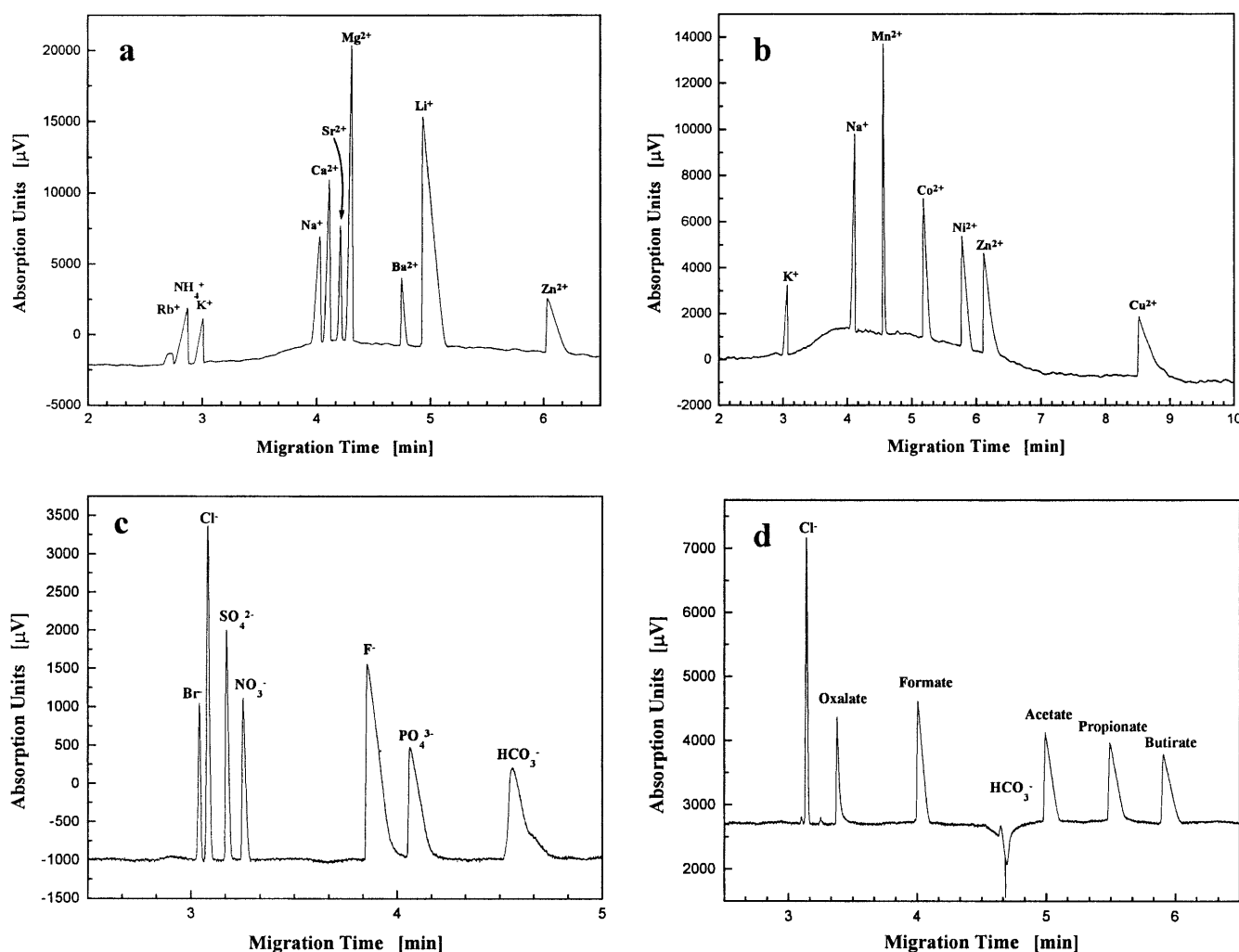
suitable groups, which cover the negatively charged silanol groups by positively charged functional groups. Most are commercially available as preparations for the CE. A reversal of the polarity of the external voltage then allows the migration, separation and detection of anionic species with the same basic instrumentation.

Chemical and instrumental parameters

CE analyses were carried out with a Waters Quanta 4000 instrument. A digital to analogue converter and vendor-provided software assured a smooth sampling of data and their storage on an IBM-compatible PC. Sampling of the UV detector output was set at 50 Hz or 0.02-s intervals.

Fig. 5

Electropherograms of standard solutions: peak concentrations are 5 mg/l for each species. **a, b** Cations. **c, d** Anions. Carrier electrolyte for cations: 10 mM pyridin, 25 mM glycolic acid, 1 mM 18-crown-6 ether. Carrier electrolyte for anions: 5 mM sodium chromate, 4% *n*-butanol, 0.1 mM OFM (Q⁺)-anion-BT, pH=8.0. Capillary: fused silica, 75 μ m \times 60 cm. Separation voltages: Cations: +25 kV; Anions: -20 kV. The samples were introduced by hydrostatic injection for 30 s at 10 cm height



For the preparation of electrolytes, sample dilutions, standards and for cleaning containers and vials only deionized water supplied by a Milli-Q system (Millipore, Bedford, MA) was used. The water blank was routinely checked for contamination and, at present, varies between 0.5 and 1 ppb of K, Na and Ca. Standard solutions were prepared from 1000 ppm stock solutions made from pure chemicals.

A series of tests were carried out to determine the most suitable electrolyte for cation separations. Following the suggestions by (Lee and Lin 1994), pyridine was found to be a universally applicable co-ion. For the conditions of a 60-cm long capillary and average separation voltage of 25 kV, a concentration of 10 mM was found to be optimal for base level separations of Group I and II elements and transition elements. Glycolic acid in a concentration of 25 mM was added as a general complexing agent, resulting in a pH value of ~ 4.5 . In order to separate the co-migrating cations of K^+ and NH_4^+ , a further addition of 1 mM 18 crown 6 ether to complex the K^+ cation (Jandik and Bonn 1993), was found to be sufficient. For the separation of the lanthanide elements to base level the basic pyridine electrolyte was used, but with HIBA (10 mM) as the sole complexing agent. All these electro-

lyte preparations have their maximum UV absorption at 254 nm wavelength.

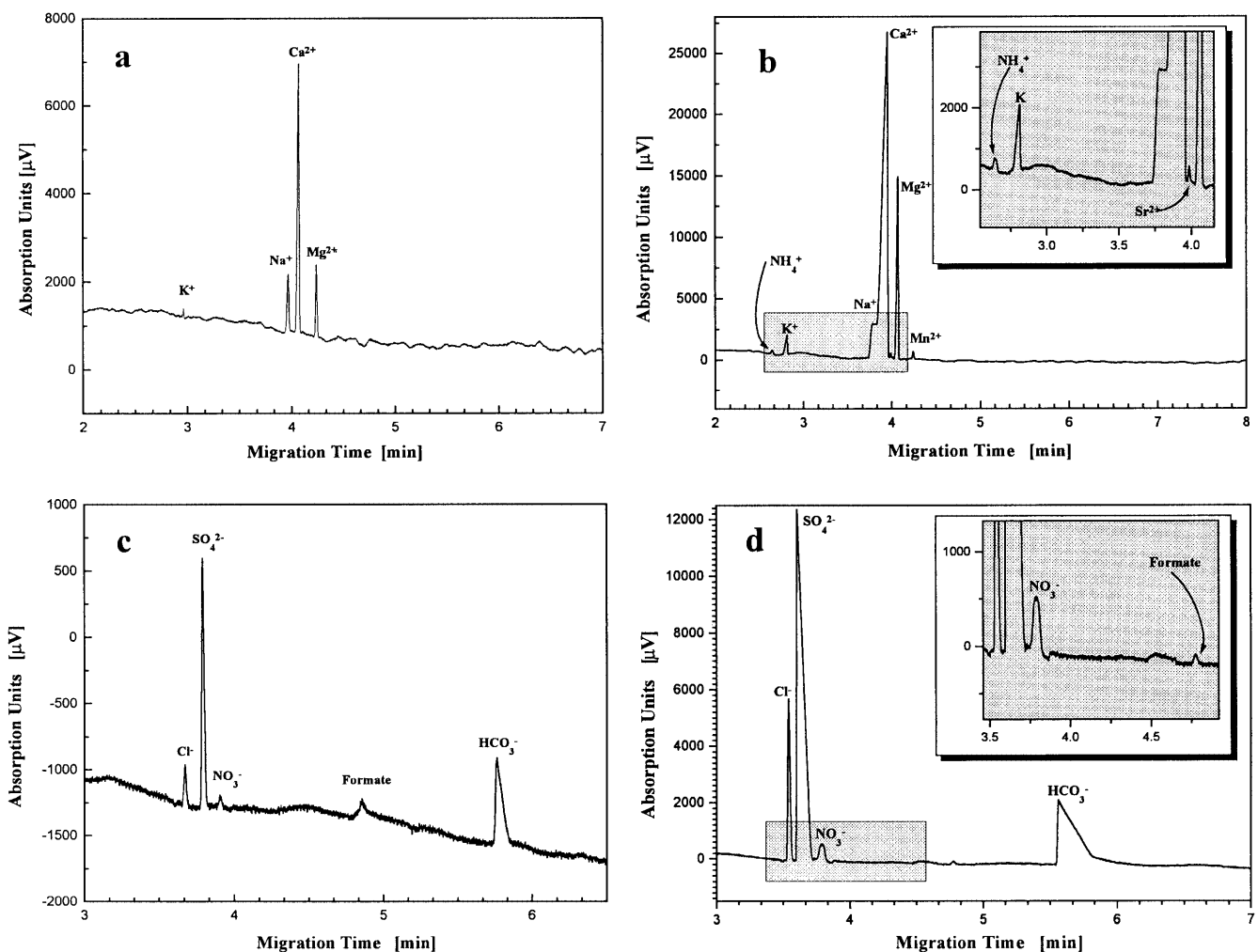
Sample electropherograms for two cation standard solutions of 5 ppm each are shown in Figs. 5a,b and, two anionic standards of 5 ppm each are illustrated in Figs. 5c,d. The sensitivity of CE separation as well as the effect of introduction by electromigration are demonstrated in Figs. 6 and 7 for water samples no. 1 and 19.

In Fig. 6b peaks for NH_4^+ , Sr^{2+} and Mn^{2+} can be discerned, and the peak for K^+ is significantly improved. Similarly, in sample s19 (Fig. 7b), NH_4^+ , Sr^+ , Zn^{2+} and Cu^{2+} could be detected by applying electromigration injection.

A separate capillary was used for the determination of anionic species and this was specially conditioned for use with an osmotic flow modifier (OFM). A convenient co-ion and chromophore is chromate (Jandik and Bonn

Fig. 6

Electropherograms of sample s1. **a, b** Cations. **c, d** Anions. Conditions as in Fig. 5. The samples were introduced by hydrostatic injection as before and, by electromigration for 10 s at 4 kV (**b, d**). Peak concentrations are presented in Table 1



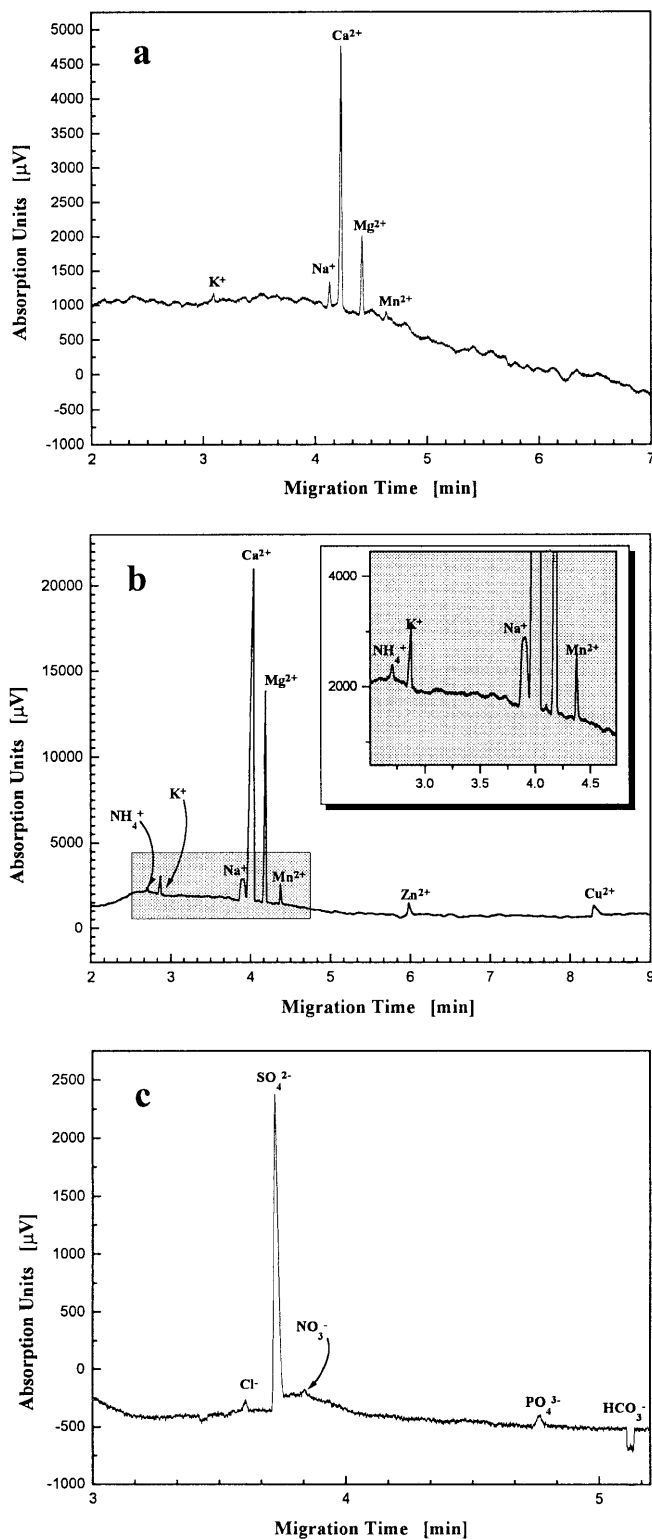


Fig. 7

Electropherograms of sample s19. **a, b** Cations. **c** Anions. Conditions as in Fig. 5. The samples were introduced by hydrostatic injection (**a, c**) and by electromigration for 10 s at 4 kV (**b**). Peak concentrations are presented in Table 1.

1993). It is prepared from sodium chromate tetra hydrate as a 5-mM solution with a pH of ~ 8.0 , adjusted by sulphuric acid. In the original formula the OFM was added at a concentration of 0.5 mM (CIA-Pak OFM anion BT, Waters). Because the OFM is a bromide salt, a small residual Br peak could sometimes be noted. By reducing the OFM concentration to 0.05 mM and adding 4% l-Butanol as stabilizer (Benz and Fritz 1994), an electrolyte without the formation of the residual Br peak was obtained. Best separations were achieved at -20 kV.

All standards were prepared by diluting 1000 ppm stock solutions containing the individual ionic species. Concentrated standards were made up from their salts, which were of analytical grade or better. Three standard levels were used for each introduction type in order to obtain smooth calibration curves.

All quantitative calculations are based on peak area integrations. Very good linear regression fits are normal for standards introduced in the hydrostatic mode. However, it should be noted that the physical nature of electromigrative introduction produces a non-linear fit, usually of the nature $y = a + b \ln(x)$.

Results and discussion

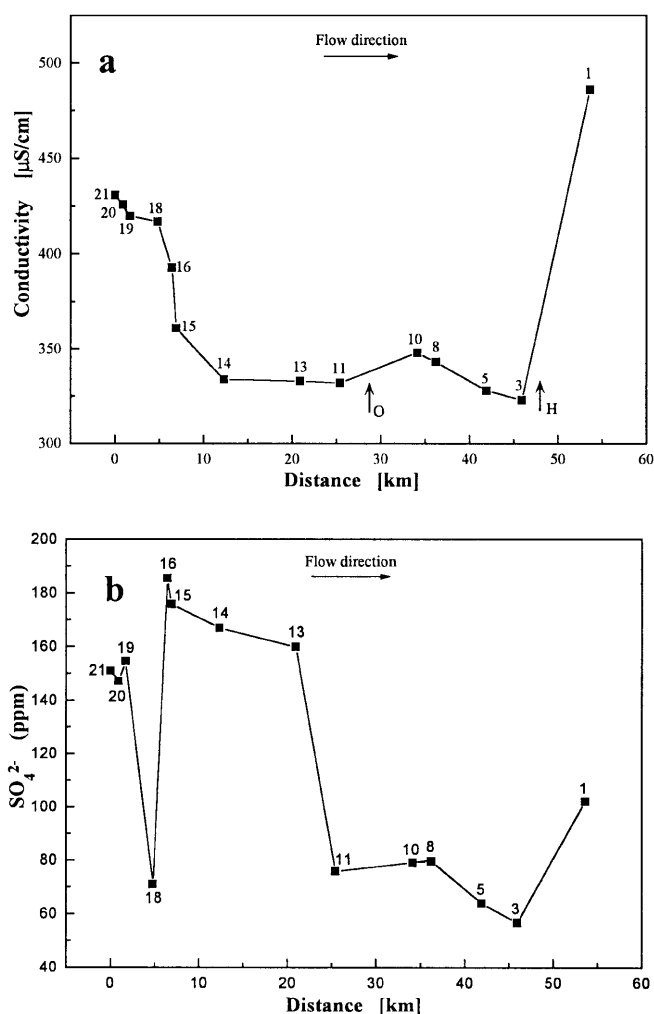
The analytical data obtained on the water samples collected from Ariesului Valley are presented in Table 1. Their chemical composition can be related to some complex processes of regional water-rock interaction and, importantly, the inflow of effluents from mining sources that led to the pollution of the river.

In the Baia de Aries mining area, the electric conductivity (EC) is higher (~ 425 $\mu\text{S}/\text{cm}$), than downstream (Fig. 8a), except for the Cheia locality. Here the influence of the water from Hasdate Brook is apparent. Changes in the composition of river water are often caused by dilution (Stollenwerk 1994). In the studied area, dilution is assumed to be mainly the result of the contribution of the left tributaries in the upper region of the Aries River. Besides dilution, some other processes, such as adsorption, absorption, chemical precipitation and complexing, are likely to occur, which could lead to changes in the composition of the surface waters.

SO_4^{2-} distribution along the Aries River can be connected to the location of mining works (Fig. 8b). The most important inputs are related to the settling ponds from Harmanesei Valley, as well as to those from Brezesti, although the latter is not active anymore. Less significant is the contribution of inflows from Sartesului Valley. The decrease of SO_4^{2-} concentration is mainly caused by the dilution and not to the chemical reactions between SO_4^{2-} and Ca^{2+} , which could lead to the formation of CaSO_4 and precipitation as gypsum. The ion activity product for CaSO_4 , along the river never exceeds a value of 2×10^{-8} , which is well below the saturation level of $10^{-4.5}$ for anhydrite. The SO_4^{2-} concentration in the river waters also directly depends on the lithology of the re-

Table 1Chemical composition of waters from the Aries River. *Acet** Acetate; *Oxal** oxalate; *Form** formate; *Buth** butyrate

Sam- ple	pH	EC μS/cm	Concentration (mg/l)																				
			Ca	Mg	Na	K	Sr	Mn	NH ₄	Ba	Zn	Cu	Cl	SO ₄	NO ₃	HCO ₃	F	Br	PO ₄	Acet*	Oxal*	Form*	Buth*
1	7.5	486	73	8.6	15.6	4.5	0.164	0.207	0.084	-	-	-	12.0	102	3.3	210	-	-	-	-	-	8.3	-
3	7.5	323	47	6.3	7.4	3.2	0.147	0.216	0.088	-	-	-	5.9	57	3.8	177	-	-	-	-	-	-	7.9
5	7.4	328	49	7.1	7.3	1.0	0.147	0.229	0.081	-	-	-	6.3	64	2.7	162	-	-	-	-	-	-	13.7
8	7.4	343	46	6.2	7.0	2.5	0.148	0.251	0.093	-	-	-	5.1	80	2.8	137	0.119	-	-	-	-	-	-
10	7.1	348	49	6.9	8.2	1.5	0.148	0.274	0.096	-	0.175	-	4.0	79	2.5	117	-	-	-	-	-	-	-
11	7.1	332	47	7.2	6.1	1.6	0.148	0.279	0.091	-	0.172	-	5.1	76	4.0	116	-	-	-	-	-	-	-
13	7.4	333	42	6.3	5.6	1.6	0.147	0.278	0.086	-	0.181	-	8.8	160	5.2	163	0.123	-	-	-	-	-	-
14	6.2	334	43	5.5	8.5	1.5	0.145	0.264	0.093	-	0.196	-	7.9	167	6.0	192	-	-	-	-	-	-	-
15	6.0	361	44	5.8	7.3	1.8	0.149	0.261	0.097	-	0.236	0.227	10.6	176	6.6	241	-	-	-	-	-	-	-
16	5.8	393	45	7.4	7.3	2.7	0.147	0.272	0.104	0.174	0.235	0.319	9.8	185	4.9	284	-	-	-	-	-	-	-
18	5.8	417	46	6.6	7.2	2.7	0.145	0.280	0.098	0.190	0.213	0.340	3.4	71	-	108	-	0.210	-	-	10.1	-	-
19	5.5	420	43	6.6	4.4	3.0	0.146	0.284	0.082	-	0.237	0.350	2.3	155	3.0	19.3	-	-	1.4	-	-	6.4	-
20	5.3	426	40	7.0	4.0	1.8	0.147	1.000	0.084	-	0.256	0.406	4.3	147	5.6	35.7	-	-	-	0.697	-	-	-
21	5.3	431	42	7.2	4.3	2.3	0.142	2.000	0.089	-	0.236	0.324	2.4	151	2.1	-	-	-	-	-	-	-	-

**Fig. 8**

Variation of conductivity and SO₄²⁻ concentrations along the Aries River from Muncle to Cheia. O Inflow of Oclis Brook; H Inflow of Hasdate Brook

gion. This is shown by an increase of the SO₄²⁻ concentrations between sample points 3 and 1. The main cause for this rise in concentration is the rock-water interaction between the Aries River water and the Neogene sedimentary rocks, which contain gypsum. In the Cheia area an open pit for gypsum extraction is still operating. In comparison, Stallard (1980) measured 1.7 mg/l SO₄²⁻ in the waters of the Amazon River in unpolluted areas, whereas Zhang and others (1990) found up to 71.7 mg/l in Yellow River waters (China). A comparison of the contents for major anions in the Aries River and three other European rivers is presented in Fig. 9. The high load of SO₄²⁻ for the Aries River is apparent and indicates the negative influences of mining operations along the Ariesului Valley.

The increase of the K⁺ concentration is significant in the Baia de Aries area and downstream (sampling points 8, 3 and 1, Fig. 10a). Water-rock interaction with hydrothermal, and potassic alteration suites of andesitic rocks in the Baia de Aries area is probably the cause of this. The source of K⁺ would then be the weathering of the alteration suite, i.e. the feldspars and micas. In the neighbourhood of sampling point 8, the local increase of K⁺ content is interpreted to be caused by the alteration of metamorphic rocks (mica-schists, sericitic-chloritic schists and amphibolites). A noticeable higher input of K⁺ was also registered in the region where Aries River crosses the complex of ophiolitic rocks.

The concentration of Mn²⁺ is very high (2000 μg/l) upstream next to Baia de Aries, and then decreases extremely fast to 203–284 μg/l over a short distance along the river in a downstream direction (Fig. 10b). Mn²⁺ is present in solution at pH values of ~7.6 (Stumm and Morgan 1981). It is thus very mobile in surface waters. The fast decrease of Mn²⁺ between sampling points 21 and 19 could be explained by adsorption phenomena on iron hydroxides present in the riverbed and, could perhaps be related to the drastic change of the redox system beyond sampling point 20.

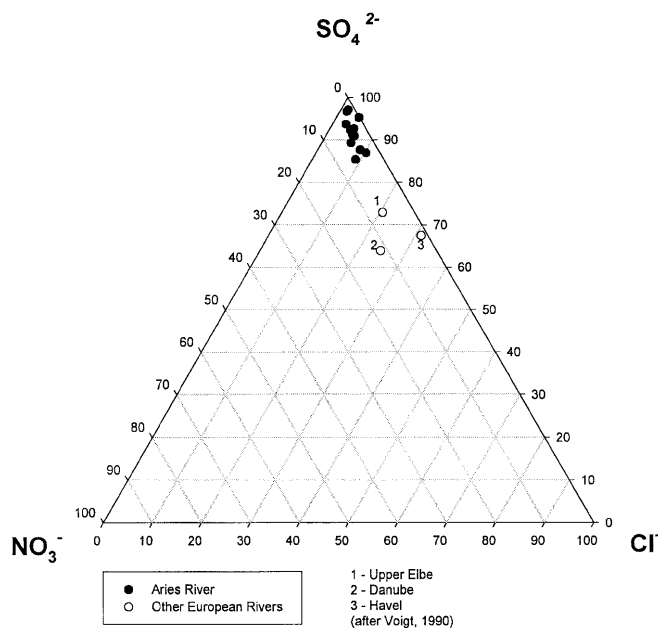


Fig. 9

Ternary diagram showing the relative concentration for Cl^- , SO_4^{2-} and NO_3^- for water from the Arises River and selected European rivers

Reported Mn^{2+} contents in river waters vary considerably. According to Martin and Whitfield (1983), the mean value of Mn^{2+} in unpolluted waters is $\sim 8.2 \mu\text{g/l}$. In Sardinia (Italy), the water of a river located in a mining region contained variable amounts of Mn^{2+} (between 3 and $643 \mu\text{g/l}$, with an average value of $139 \mu\text{g/l}$) (Cabo and others 1992). Konhauser and others (1997) measured the Mn^{2+} content of a river in India and found higher values, between 19.3 and $459.4 \mu\text{g/l}$ (the average value was $144.6 \mu\text{g/l}$). In comparison, the values in Table 1 indicate a significant pollution of Mn^{2+} as a result of the mining activities in Rosia Poieni and Baia de Aries areas. The concentration of Cu^{2+} in the Aries River near Baia de Aries is $\sim 320 \mu\text{g/l}$. A higher concentration of $406 \mu\text{g/l}$ was noticed at sampling point 20 (Fig. 10c). The increase in Cu concentration is related to the presence of a settling pond in Harmaneasa Valley. Downstream from sampling point 19 the amount of Cu decreases rapidly, and downstream of sampling point 14 the concentration is below the detection limit of $\sim 20 \mu\text{g/l}$.

Under normal circumstances, Cu^{2+} is adsorbed onto iron hydroxides, which are present in small quantities in the streambed. Adsorption starts at a pH of ~ 5 (Papp and Kümmel 1992), whereas at neutral pH values, Cu^{2+} concentrations in solution are very low (Kelly and others 1988b). Cu precipitates as hydroxide at a pH of ~ 7.2 (Kelly and others 1988a). Because of the relatively low pH of the Aries River in places, the main process, which is responsible for the decrease of Cu concentration, could be adsorption. The presence of iron hydroxides precipitated from AMD by oxygenation can significantly modify the amount of Cu^{2+} in solution because of adsorption

processes, as mentioned in several papers (Laxen 1984; Johnson 1986; Kooner 1993; Grossi and others 1994). The presence of iron hydroxides in the Aries River in the vicinity of the Baia de Aries mining area is shown by the brownish-reddish crust that covers the surface of pebbles. In unpolluted waters, dissolved Cu^{2+} concentrations in rivers have been reported to be between $0.38\text{--}2.35 \mu\text{g/l}$ (Boyle 1979). The very high concentrations of Cu^{2+} in the Aries River clearly indicate a strong degree of pollution. The main source of Cu^{2+} is the Rosia Poieni quarry, located at $\sim 12 \text{ km}$ upstream from Baia de Aries and, to a lesser degree, the mining works from Baia de Aries. Zn is a very mobile element in many environments (Kelly and others 1988b; Papp and Kümmel 1992). In the studied area, the Zn^{2+} concentration varies from 172 to $256 \mu\text{g/l}$ (Table 1). A comparison between the distributions of Cu^{2+} (Fig. 10c) and Zn^{2+} (Fig. 10d) supports a contention of the high mobility of the latter as mentioned by several authors (Kelly and others 1988b; Papp and Kümmel 1992). Downstream of sampling point 15, at a pH of 6, there is a continuous decrease in Zn^{2+} concentration. When the pH reaches a value of 7.4, the Zn^{2+} concentration decreases below the detection limit. As in the case of Cu^{2+} , an increase in Zn^{2+} content is registered at sampling point 20 because of the input of the metal from the settling pond from Harmaneasei Valley (Fig. 3). At sampling points 16 and 15, the increase of Zn^{2+} is caused by the input of effluents that originate in the settling ponds of Brezesti and Sartesului Valley (Fig. 3).

At pH values between 6 and 8, the main chemical species of Zn is the $2+$ cation in solution (Hem 1972; Vuceta and Morgan 1978). Within these limits, dilution and adsorption processes, more than chemical precipitation, control the Zn^{2+} concentration of the Aries River in the studied area. At pH values of 6, the adsorption of Zn^{2+} onto the surface of iron hydroxides is very low (Florence 1980; Papp and Kümmel 1992), but at higher values the process becomes more significant (Johnson 1986; Papp and Kümmel 1992).

According to Shiller and Boyle (1985) filtered water samples contain between 0.02 and $1.8 \mu\text{g/l}$ Zn^{2+} , while in the polluted areas the mean Zn^{2+} content is between 0.07 and $15.6 \mu\text{g/l}$. Unpolluted waters were reported to contain $\sim 11 \mu\text{g/l}$, whereas Elderfield and others (1971) and Abdullah and Royle (1972) report an average Zn^{2+} concentration in river waters of $24 \mu\text{g/l}$. Comparing these data with the values in Table 1, a significant pollution of the Aries river is demonstrated.

With the analytical technique employed, no traces of Fe^{2+} and Al^{3+} could be recorded, in spite of the fact that these elements are quite common in water polluted by mining activities. In primary sulphide ores, the elements in minerals are present mainly in the reduced form (Wiggering 1993). When minerals get in contact with the atmosphere they become oxidized. Thus Fe^{2+} , which is unstable in solution, is oxidized to Fe^{3+} . It then becomes unstable under higher pH conditions and is precipitated as iron hydroxide. According to Skelly and Loy

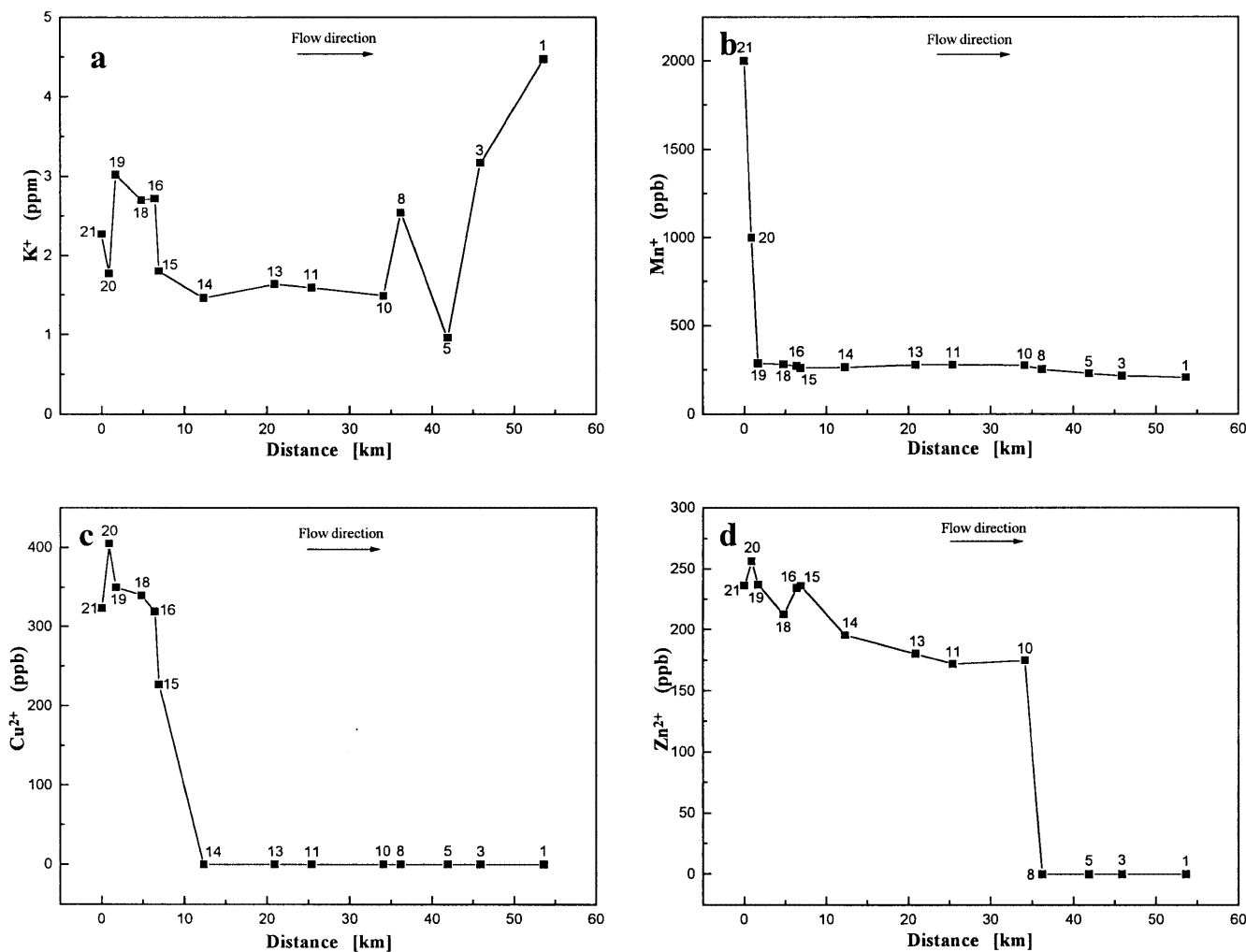


Fig. 10

Variation of the concentrations for some cations in water along the flow of the Aries River. Numbers indicate the sample locations on the riverbank

(1973), the critical pH values are ~ 4.3 for Fe^{3+} and 5.2 for Al. In the Baia de Aries mining area, the brown crust, which covers the pebbles on the riversides, indicates the presence of iron hydroxides. Because of pH values higher than the critical ones, Fe^{3+} and Al precipitate, thus they are no longer available in solution and not present in the measured data.

Conclusions

In this paper, the authors have tried to demonstrate that, because of its efficiency and resolution and its ease as an analytical procedure, the CE method can be applied successfully for the determination of dissolved anions and cations, as well as for the analysis of organic anions from

river water. The relative low costs and the high reproducibility plead for an acceptance of the CE method in water pollution control as compared with other methods. The results show the evolution of the Aries River water from an SO_4^{2-} contaminated, slightly acidic water to a condition where, by successive leaching of carbonate (Fig. 11a), the composition of the river water changes to a more neutral stage. The changes in the anionic composition along its flow are greater than those in its cationic contents (Fig. 11b).

From the study it is also apparent that the degree of pollution caused by mining activities in the drainage area of the Aries River is correlated to

1. specific features of the ores mined in the region (e.g. sulphides of Cu, Zn and carbonates);
2. the type of the host-rock and country rock (carbonate rocks, andesites and others); and
3. the methods of exploitation used.

The oxidation of sulphides does not generate acidic waters from the mines of Baisoara and Baia de Aries because of the high amount of calcite in the gangue. However, for the ores from Baia de Aries (the vein-type mineralization) and those from Rosia Poieni, because of the low amount of buffer minerals (especially calcite), the

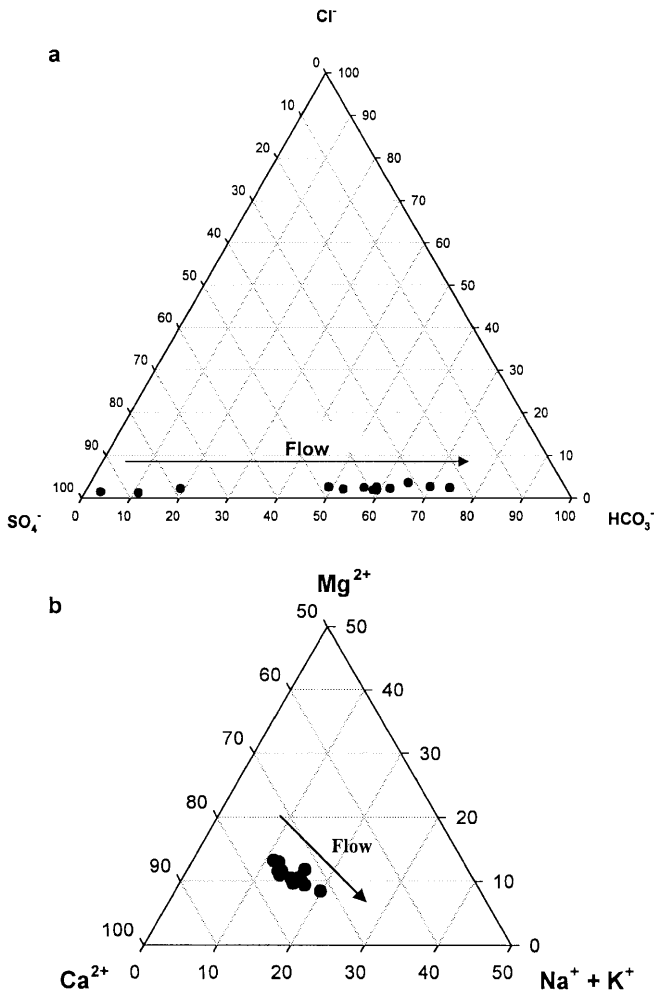


Fig. 11

Ternary diagram of the major a anionic species and b cationic species in the Aries River

same process of oxidation gives rise to acid drainage, waters with low pH values and high amounts of dissolved metals.

Local variations in the concentration of different elements, in addition, point to a source of pollution identified as the settling ponds from Harmanesei Valley, Sartasului Valley and Brezesti. Apart from the pollution caused by mining activities some local sources of pollution were recognized, such as the input of domestic and agricultural effluents in the vicinity of the settlements along the riverbanks.

Several processes: water-rock interaction, and chemical reactions at the junction of Aries river with other tributary systems of different composition and adsorption patterns contribute in a significant way to the modification of the chemical composition of the water of the Aries River.

Zn, because of its high mobility, migrates far from its source. The variation of Zn²⁺ concentrations in the filtered fractions of the water is apparently controlled by

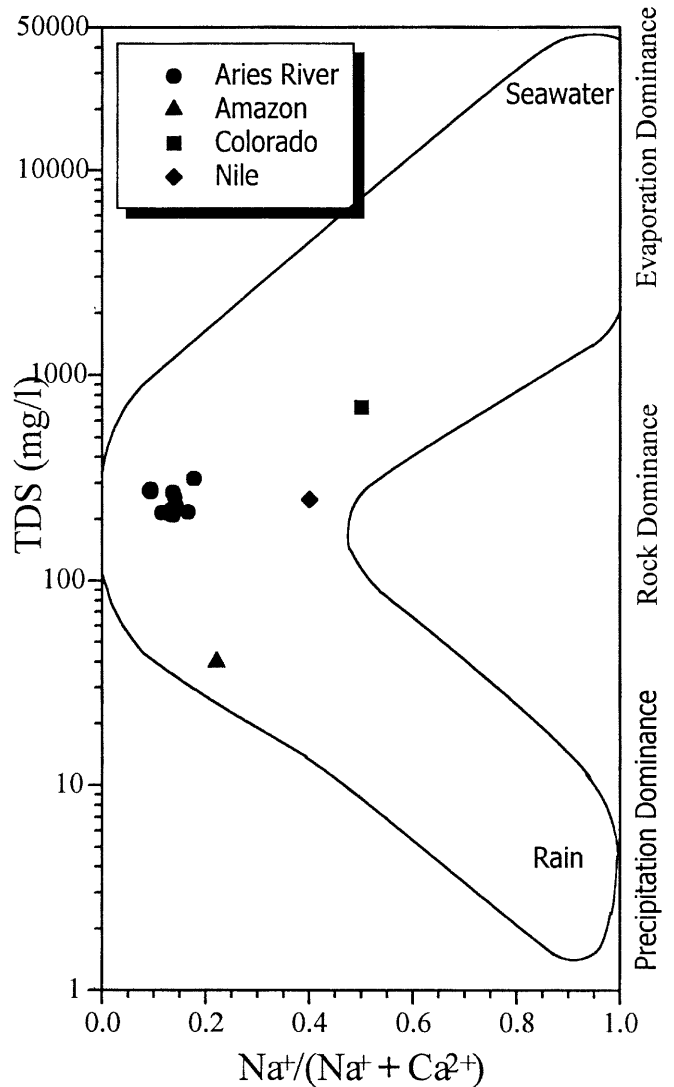


Fig. 12

The classification of surface waters according to Gibbs (1970), showing some major stream systems [concentration data: Amazon from Stallard (1980); Colorado and Nile from Meybeck (1979)] as well as the position of the Aries River

adsorption phenomena, at pH values >6. The active and inactive settling ponds also have a major influence on Zn²⁺ concentration. The waters of the Aries River, by comparison, contain concentrations of Cu²⁺ and Zn²⁺ that are up to 100 times higher than those of unpolluted river water.

Compared with larger river systems worldwide (Fig. 12), the Aries River has a high degree of water-rock interaction and pollution. In this classification (Gibbs 1970) it shows a relatively high amount of TDS, yet a low content of Na⁺.

References

- ABDULLAH MI, ROYLE LG (1972) Heavy metal content of some rivers and lakes in Wales. *Nature* (London) 238:329–330
- BENZ NJ, FRITZ JS (1994) Studies on the determination of inorganic anions by capillary electrophoresis. *J Chromatogr* 671:437–443
- BODEN J, BÄCHMANN K (1996) Investigation of matrix effects in capillary zone electrophoresis. *J Chromatogr* 734:319–330
- BOYLE EA (1979) Copper in natural waters. In: Nriagu JO (ed) *Copper in the environment, Part 1: Ecological cycling*. Wiley-Interscience, New York
- CABOI R, CIDU R, CRISTINI A, FANFANI L, NOVELLI RM, ZUDAS P (1992) Metal contamination of stream waters from former mining activity. In: Kharaka YK, Maest AS (eds) *Water-rock interaction, Proceeding of the 7th International Symposium on Water-Rock Interaction, Park City, Utah, 13–18 July 1992, vol 1, Low temperature environments*, A.A. Balkema, Rotterdam
- DABEK-ZLOTORZYNSKA E, DLOUHY JF (1994) Application of capillary electrophoresis in aerosol analysis: determination of inorganic and organic anions. *J Chromatogr* 671:389–395
- DABEK-ZLOTORZYNSKA E, PIECHOWSKI M, LIU F, KENNEDY S AND DLOUHY JF (1997) Routine determination of major anions in atmospheric aerosols by capillary electrophoresis. *J Chromatogr* 770(1–2):349–359
- DURKIN TV, HERRMANN JG (1996) Introduction: focusing on the problem of mining wastes. In: US EPA (ed) *Managing environmental problems at inactive and abandoned metals mine sites*, Seminar publication EPA/625/R-95/007, US Environmental Protection Agency, Cincinnati
- ELDERFIELD H, THORNTON I, WEBB JS (1971) Heavy metals and oyster culture in Wales. *Mar Poll Bull* 2:44–47
- FLORENCE TM (1980) Speciation of zinc in natural waters. In: Nriagu JO (ed) *Zinc in the environment, Part 1: Ecological cycling*. Wiley-Interscience, New York
- GIBBS, RJ (1970) Mechanisms controlling world water chemistry. *Science* 170:1088–1090
- GRÄBER G, FRIMMEL FH (1996) Reaction von Sedimenten unterschiedlicher Herkunft unter oxidierenden Bedingungen in Abhängigkeit von pH-Wert. *Acta Hydrochim Hydrobiol* 24(4):161–167
- GROSSI PR, SPARKS DL, AINSWORTH CC (1994) Rapid kinetics of Cu(II) adsorption/desorption on goethite. *Environ Sci Technol* 28:1422–1429
- HALLBAUER DK (1994) Geochemical trace element analysis for ionic species by capillary electrophoresis. *Min Mag* 58A(VM Goldschmidt Conference Abstracts):362–363
- HALLBAUER DK (1997) The application of capillary ion analysis to the geochemistry of natural aqueous fluids and in particular to the analysis of fluid inclusions in minerals. In: Pei Rongfu (ed) *Energy and mineral resources for the 21st century: geology of mineral deposits, mineral economics*, Proceedings of the 30th International Geological Congress, vol 9, ISBN 90-6764-264-9, pp 409–424
- HALLBAUER DK, CHEVALLIER L, WOODFORD A (1995) The application of capillary ion analysis to the geochemistry of ground water from western Karoo aquifers. Conference paper no 43, ISBN 0-620-19572-X. *Groundwater '95*. Conference on groundwater recharge and rural water supply, Midrand, SA, 26–28 September 1995
- HEM JD (1972) Chemistry and occurrence of cadmium and zinc in surface water and groundwater. *Water Resource Res* 8:661–679
- HERR C, GRAY NF (1997) Sampling riverine sediments impacted by acid mine drainage: problems and solutions. *Environ Geol* 29(1/2):37–45
- IONESCU O (1974) Mineralizatia cuprifera de tip diseminat de la Rosia – Poieni (jud. Alba). *St. cerc geol geofiz geogr geologie* 19:77–84
- IONESCU O, SOARE C, GHEORGHIU M (1975) Contributii la cunoasterea zacamintului cuprifera Rosia-Poieni. *Alteratii hipogene*. *St cerc geol geofiz geogr geologie* 20/2:159–170
- JANDIK P, BONN G (1993) *Capillary electrophoresis of small molecules and ions*. VCH Publishers, New York
- JOHNSON CA (1986) The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage: the adsorption of Cu and Zn on amorphous Fe oxyhydroxides. *Geochim Cosmochim Acta* 50:2433–2438
- KELLY M, ALLISON WJ, GARMAN AR, SYMON CJ (1988a) Acid mine drainage in the aquatic environment. In: Kelly M (ed) *Mining and the freshwater environment*. Elsevier Applied Science, London
- KELLY M, ALLISON WJ, GARMAN AR, SYMON CJ (1988b) Heavy metals in the aquatic environment. In: Kelly M (ed) *Mining and the freshwater environment*. Elsevier Applied Science, London
- KONHAUSER KO, POWELL MA, FYFE WS, LONGSTAFFE FJ, TRIPATHY S (1997) Trace element chemistry of major rivers in Orissa State, India. *Environ Geol* 29(1/2):132–141
- KOONER ZS (1993) Comparative study of adsorption behavior of copper, lead, and zinc onto goethite in aqueous systems. *Environ Geol* 21:242–250
- LAXEN DPH (1984) Adsorption of cadmium, lead, and copper during the precipitation of hydrous ferric oxide in a natural water. *Chem Geol* 47:321–332
- LAZAR C (1966) Contributii la cunoasterea zacamintului polimetalic de la Baia de Aries (Muntii Apuseni) *St cerc geol geofiz geogr* 11/2:403–415
- LAZAR C, INTORSUREANU I, POPESCU M (1972) Studiul petrografic al rocilor banatitice din zona Masca – Baisoara (Muntii Apuseni) *DS Inst Geol LVIII(1):144–173*
- LEE YH, LIN TI (1994) Determination of metal cations by capillary electrophoresis – effect of background carrier and complexing agents. *J Chromatogr* 675:227–236
- MARTIN JM, WHITFIELD M (1983) The significance of the river input of chemical elements to the ocean. In: Wong S, Boyle E, Bruland KW, Burton JD, Golberg ED (eds) *Trace metals in seawater*, vol C, Plenum, New York, pp 265–296
- MEYBECK M (1979) Concentration des eaux fluviales en éléments majeurs et apports en solution aux océans. *Rev Géol Dyn Géogr Phys* 21:215–246
- PAPP S, KÜMMEL R (1992) Az elemek környezeti kemiaja. In: Papp S, Kümmel R (eds) *Környezeti kémia*. Tankönyvkiadó, Budapest, pp 185–275
- RADULESCU D, DIMITRESCU R (1966) *Mineralogia topografica a Romaniei*. Acad Rom, Bucuresti
- ROBERTSON A MACG (1996) The importance of site characterization for remediation of abandoned mine lands. In: US EPA (ed) *Managing environmental problems at inactive and abandoned metals mine sites*, Seminar Publication EPA/625/R-95/007, US Environmental Protection Agency, Cincinnati
- SHILLER AM, BOYLE E (1985) Dissolved zinc in rivers. *Nature* (London) 317:49–52
- SKELLY AND LOY (Consultants) and Pennsylvania Environmental Consultants (1973) *Processes, procedures and methods to control pollution from mining activities: surface mining*. EPA Publication No. EPA-430/9-73-011, Washington
- STALLARD RF (1980) Major element geochemistry of the Amazon River system. PhD Thesis, MIT, Cambridge, MA

- STEFAN A, LAZAR C, BERBELEAC I, UDUBASA G (1988) Evolution of banatitic magmatism in the Apuseni Mts and associated metallogenesis. *DS Inst Geol* 72-73/2:195-213
- STOLLENWERK KG (1994) Geochemical interactions between constituents in acidic ground water and alluvium in an aquifer near Globe, Arizona. *Appl Geochem* 9:353-369
- STUMM W, MORGAN JJ (1981) Oxidation and reduction. In: Stumm W (ed) *Aquatic chemistry*. John Wiley & Sons, New York, pp 418-503
- UDUBASA G, ILINCA G, MARINCEA S, SABAU G, RADAN S (1992a) Minerals in Romania: the state of the art 1991. *Rom J Mineral* 75:1-51
- UDUBASA G, STRUSIEVICZ RO, DAFIN E, VERDES G (1992b) Mineral occurrences in the Metaliferi Mountains (Excursion guide). *Rom J Mineral* 75(2):3-35
- VLAD S (1983) Porphyry copper deposits of Romania. In: Vlad S (ed) *Geology of porphyry copper deposits (in Romanian)*. Edit Acad RSR, Bucuresti, pp 125-142
- VUCETA J, MORGAN JJ (1978) Chemical modeling of trace metals in fresh waters: role of complexation and adsorption. *Environ Sci Technol* 12:1302-1309
- WIEDER RK, NOVÁK M (1995) Biogeochemical processes during the treatment of acid mine drainage: the Kentucky wetland project. In: Pašava J, Krribek B, Zák K (eds) *Mineral deposits: from their origin to their environmental impacts*, Proceedings of the third biennial SGA meeting, Prague, 28-31 Aug 1995, AA Balkema, Rotterdam
- WIGGERING H (1993) Sulfide oxidation - an environmental problem within colliery spoil dumps. *Environmental Geology* 22:99-105
- ZHANG JW, HUANG W, LIN MG, ZHON A (1990) Drainage basin weathering and major element transport of two large Chinese rivers (Hwanghe and Changjiang). *J Geophys Res* 95:13277-13288