

Geochemical trace element analysis for ionic species by capillary electrophoresis

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Simultaneously with great improvements in analytical techniques during the last two decades data have become available on trace elements in minerals which have caused geochemists to attach less importance to bulk analyses. The statistical distribution of trace elements in minerals from single grain analyses, 'fingerprinting' of minerals by trace elements, the identification of pathfinder elements and minerals and other applications have been published in increasing numbers.

The partitioning of elements between minerals and fluids has also been found by many geochemists to be of great importance in tracing and characterizing geochemical processes.

Particular examples are the rare earth elements (REE) as tracers of geochemical processes, and various anions and anionic complexes as transport agents of chemical elements, especially metals in ore deposits, through the Earth's crust.

Many analytical techniques were developed which allowed a drastic reduction in sample size combined with a lowering of detection limits. Some of them are costly, time consuming and not always applicable to the elements of interest (e.g. INNA, AAS, ICP). However, the application of these techniques to the geochemistry of single mineral grains, and the subsequent statistical analysis of data, have led to new insights into the nature and behaviour of geochemical systems as well as to the practical use of minerals as geochemical pathfinders.

Over the past few years a new analytical technique, Capillary Electrophoresis or Capillary Ion Analysis (CIA), has been developed, and is now available as compact, highly efficient and cost effective instrumentation. The technique applies capillary electrophoresis combined with indirect UV photometric detection to the analysis of anions and cations in small samples (ml to μ l range of analytes). Of particular interest to the field of geochemistry is its matrix independence and the simultaneous determination of REE together with other elements, thus eliminating time-consuming preparations. The output of the UV detector is typically sampled at a 0.02 second interval, and is available in digitized form. Combined with a low background and a superior peak shape, separation efficiencies of between 200000 and 1 million theoretical plates can be achieved. The use of electro-migration as a method to introduce analyte material into the capillary can shift the detection limits for some ionic complexes into the parts-per-trillion range (typically about 35 ppt for Li^+).

As an example of current research interests, the soluble (or leachable) anions and cations in selected Witwatersrand single quartz pebbles, in quartz from porphyry deposits and pegmatites as well as the ionic composition of water from some hot springs, were determined by CIA.

Samples of leachate from 1g each of crushed quartz samples were prepared and analyzed for

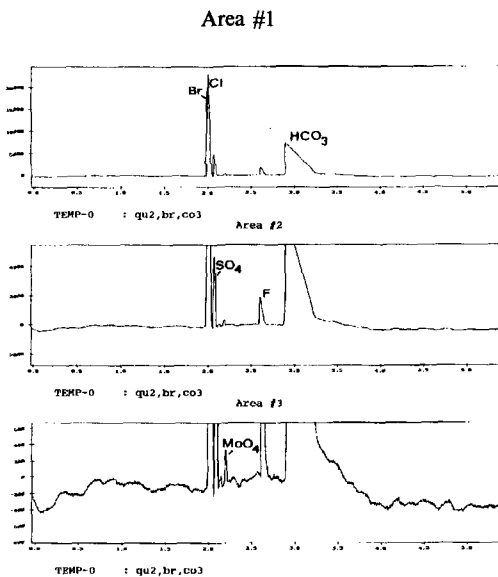


FIG. 1. Original and expanded versions of an electropherogram of a quartz leachate, spiked with 2 ppm Br^- & HCO_3^- as markers. Vein quartz from the Vlădeasa granite, Romania, containing 20 ppb of MoO_4^{2-} . Conditions: capillary, 60 cm \times 75 cm, fused silica. 5 mM chromite electrolyte with osmotic flow modifier 'Anion BT' at pH 8.0. Electromigration 20 sec at 5 kV. Indirect UV detection at 254 nm. The abscissa represents migration time (min.), the ordinate is in absorption units (uV).

Cl^- , F^- , SO_4^{2-} , NO_3^- , HPO_4^{2-} and HCO_3^- . Concentrations (calculated for the original sample mass) for chloride, sulphate, nitrate and fluoride in the range from 0.7 ppm (for F^-) to 3.3 ppm (for Cl^-) were found in reef quartz (Fig. 1). Similar ranges were found for cations such as Na, K, Ca, Ba, Li and Zn.

In another application of the technique, samples of quartz from veins in the granite from the Vladeasa Mountains, Romania was crushed, leached and analysed for anions. Using a 1 g sample of clean quartz, an amount of 20 ppb MoO_4^{2-} could be determined in the presence of the major components Cl^- , SO_4^{2-} and F^- (Fig. 1.).

The results compare well with the analysis of

similar samples using Ion Chromatography (IC) instrumentation. However, the time required to analyze one analyte was less than half of that used for the IC, the minimum analyte required is about 100 μl of which about 100 nl are actually used per run. The cost of chemicals are less than 1/10th. No preparations, except filtration, were necessary for water samples.

Reference

- Jandik, P. and Bonn, G. (1993) *Capillary Electrophoresis of Small Molecules and Ions*. VCH Publishers, Cambridge, 298pp.