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A Micro-Analytical Technique for Determination of Aluminum in Aqueous Solutions

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A microanalytical technique for determination of aluminum in aqueous solutions

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Abstract

A flow-cell colorimetric technique has been developed by which Al concentrations of 0.0003 to 0.1 wt. percent can be analyzed in one-microliter fluid samples. An Al-complexing reagent (Ferron) continuously flowing through teflon capillary tubing is spiked with one-microliter aliquots of solutions containing Al. The sample reacts with the reagent and subsequently passes through a microcolorimeter. Measurement of less than one nanomole Al is possible by comparing the integrated absorbance of unknown samples with standard solutions.

Introduction

Among the major elements of the earth's crust, aluminum is noted for its low concentrations in natural and experimental aqueous solutions equilibrated with common minerals. Anderson and Burnham (1967) found that the solubility of corundum in acidic hydrothermal fluids was generally below the limit of detection (0.1 weight percent). Special analytical techniques are available to detect Al concentrations on a parts per billion level (for example, May *et al.*, 1979), but these require a relatively large volume (100 ml) of solution. In order to study Al in aqueous solutions at crustal temperatures and pressures in cold-seal pressure vessels, it was necessary to develop an analytical technique that could measure low Al concentrations in microliter samples. A flow-cell colorimetric method has been developed by which Al concentrations of 0.0003 to 0.1 weight percent can be analyzed in one-microliter fluid samples. The technique is based on the colorimetric determination of Al hydroxyquinolate in a carefully buffered and mixed Ferron solution.

Procedure

The flow-cell colorimetric method entails (1) injecting and mixing a small volume of sample into a continuously flowing stream of reagent to produce a colored reaction product, (2) passing the sample–reagent mixture through the low-volume optical cell of a flow-cell colorimeter, (3) integrating the observed absorbance over the time interval of the sample spike, and (4) comparing the integrated absorbance with that of standard solutions. The advantages of this type of colorimetry include: (1) a relatively small volume of sample is required because of the small volume of the absorbance cell, (2) multiple determinations of samples and standards are facilitated by the ease of sample introduction, and (3) any time dependency of sample–reagent reactions is overcome because of the dynamic nature of the measurement. As a result of recent developments in liquid chromatography, nearly all the required equipment is now available commercially.

The details of the flow-cell system are shown in Figure 1. An Al-complexing reagent solution is pumped with approximately equal flow rates through two plastic tubes that are ultimately joined downstream. A compressed-air-operated double switch on one of the flow lines directs the flow to either a sample loop or a bypass loop (not shown) of equal length. Samples are introduced by means of a specially constructed pipette holder[2] (see inset, Fig. 1).

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[2] The pipette holder is designed to hold glass capillary pipettes so that a sealed connection may be repeatedly formed between the teflon tubing and disposable glass pipettes. The holder consists of an aluminum frame with threaded holes to support two threaded polypropylene connectors. The polypropylene connectors have central holes through which the teflon tubing is passed. Cone-shaped seats in the connectors accept the glass capillary pipettes. The entire volume of the pipettes is filled with the sample.
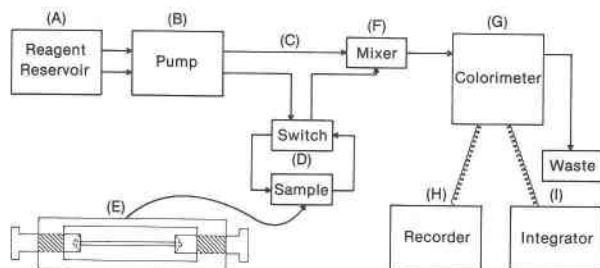
Fig. 1. Schematic diagram of the colorimeter flow system. Details of the sample pipette holder are shown in the inset. (A) Reagent is Ferron, sodium acetate, and acetic acid. (B) Gilson Minipuls 2 peristaltic pump, 0.030 in. pump tubing, pump setting = 300. (C) Zeus Industrial Products 32-guage teflon tubing. (D) Chromatronix Inc. PA-875 switches in tandem. (E) Dade Volupette pipette P4521-1. (F) Mixer and other junctions made with Gilson polypropylene connectors. (G) Gilson Holochrome UV Monitor HM/HLPC. (H) Hewlett Packard Recorder 7132A. (I) Spectra-Physics Autolab Minigrator.

When a 1-μl sample pipette is in place, the switch can direct reagent flow through the sample pipette. Mixing of sample and reagent occurs as a result of turbulence in the narrow plastic tubing (32 gauge) and in the mixing chamber (volume of 30 μl) where the two flow lines are joined. The flow passes on through a colorimeter (cell volume 20 μl) and through enough additional tubing to assure a reasonable back pres-

sure. Absorbance is monitored at 370 nm by a chart recorder and an electronic integrator.

The complex-forming reaction between Al and Ferron (8-hydroxy-7-iodo-5-quinoline sulfonic acid) is pH sensitive. Therefore, to ensure accurate results, it is necessary to buffer the Ferron solution in the neighborhood of pH = 5. Because of the relatively high HCl concentrations used in the Al solutions studied, a concentrated buffer solution (2M sodium acetate, 0.2M acetic acid) was mixed with an equal volume of the Ferron solution (0.25 g/l). With this buffered Ferron solution, a difference of an order of magnitude in HCl concentration between an unknown and the standards introduces an error of only about 2%. Because of the formation of iron hydroxyquinolate, the technique will not work (without iron extraction) for iron-bearing solutions if the iron content is unknown.

Although the absorbance peak height is a function of Al concentration, peak area has proved to be a more reliable parameter. Typical peaks from a sequence of standard solutions are shown in Figure 2. The actual shape of the peaks represents the variable dilution (average dilution = 300:1) of a non-fading sample that results from the mixing process. The peaks last for 60–90 sec and have been spaced at intervals of about 150 sec. One standard deviation from the mean of a series of replicate measurements
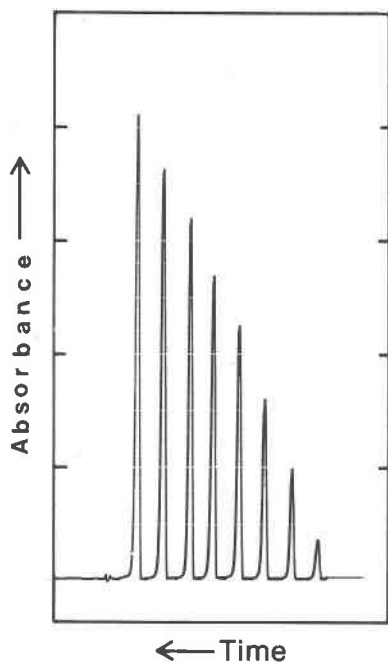

Fig. 2. Absorbance peaks for 1-μl samples containing (from right to left) 1, 3, 5, 7, 9, 11, 13, and 15 millimolar (mM) solutions of aluminum in 0.5M HCl. A distilled water sample is shown at the extreme left.
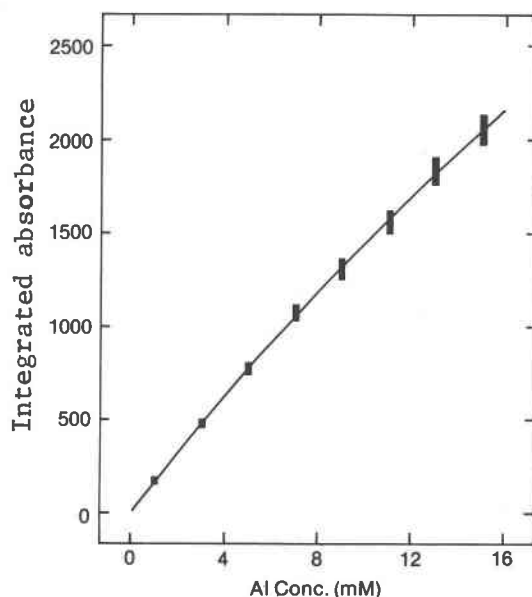

Fig. 3. A standard curve obtained from five replicate determinations of the integrated absorbance of the eight standards used for Fig. 2. The curve is a second-order fit to the data. The error bars indicate one standard deviation from the mean of the measured absorbance for each sample.

of the same sample solution is generally less than 2–3% of the peak area. In practice, four or five 1-μl samples of an unknown are alternated with the same number of each of two to four bracketing standard solutions. Although the time-integrated absorbance appears to be strictly linear with concentration only for Al concentrations below 5 mM, a linear approximation is followed up to at least 40 mM for closely bracketing standard solutions. A representative standard curve is shown in Figure 3. The high density of the buffered Ferron solution leads to additional absorbance due to optical interference fringes at both ends of a sample spike (see distilled water peak in Fig. 2). This additional absorbance limits the sensitivity of the technique to Al concentrations above 0.2 mM. Within this limit, however, measurement of less than a *nanomole* of Al in a 1-μl sample is obtainable.

Two potential problems with regard to the sample injection procedure require comment. (1) When the sample micropipette is inserted between the funnel-shaped connectors to the plastic flow line (inset, Fig. 1), an air bubble may appear in the pipette. The air bubble signifies that some of the sample solution has been sucked from the pipette, because of contact with a drop of reagent solution on the connector surface or because of an overfilled pipette. In such cases, anomalous results are obtained, mainly because there is no assurance that all the unknown solution entered the flow line. This problem can be avoided by thoroughly cleaning the connector surfaces with a blast of air or Freon between samples and by cleaning any excess solution from the sample pipette. (2) Deformation of the connectors with repeated use can increase the resistance of the sample flow line, decreasing the flow rate in that line. Periodic replacement of the connectors and monitoring of the time interval from injection to peak (30 sec) can prevent problems

of this nature. Slight variations in the sample line resistance, due for example to variations in pipette centering, are probably responsible for a significant part of the observed scattering of data.

Conclusions

The capability of analyzing Al at submicrogram levels is an important step toward the experimental determination of the nature of dissolved Al in hydrothermal fluids. Using the analytical method presented here in conjunction with techniques similar to those developed by Frantz and Eugster (1973) and Popp and Frantz (1979), one can determine both the concentration and speciation of Al in equilibrium with Al-bearing minerals at high temperatures and pressures.

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