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S O L V E N T   E X T R A C T I O N  
I N  
A N A L Y T I C A L   G E O C H E M I S T R Y

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"No man is an Iland, intire of it selfe"

(Donne, 1623)

ABSTRACT

A procedure combining solvent extraction enrichment techniques and spectrographic analysis was developed for the quantitative determination of many trace elements in a wide range of silicate rocks and in a series of highly saline Antarctic lake waters.

Since a great deal of the work depended on spectrographic analysis, an investigation was carried out to improve the precision and sensitivity of existing methods. An improved method for the determination of spectral line intensities was developed. This was based on the author's modification of the partial Seidel function, referred to as B-functions. A conversion table for these is given. A scale calibrated in B-functions was incorporated into a Hilger microphotometer enabling such values to be obtained directly without the use of conversion tables. B-values can be plotted directly on to the linear ordinate of semi-log paper if the self-calibration method is used for evaluating line intensities. This results in a straightening of the characteristic curve with an attendant time saving and an improvement in the accuracy of the background extrapolation. A nomographic technique was also developed for use in conjunction with this scale and resulted in a rapid evaluation of line intensities but with some loss in precision.

Cathode excitation as distinct from cathode-layer was compared with anode excitation under the same conditions. Data on 33 elements were used to study relative self-absorption effects, absolute sensitivities, volatilisation curves, times for complete combustion, and background effects. Data on 14 elements and 35 line pairs were used to study reproducibilities in the three matrices, NaCl,  $\text{CaCl}_2$  and carbon. It was shown that cathode excitation in a carbon matrix afforded the greatest precision for a number of the more volatile elements. Anode excitation provided generally better precision if a NaCl matrix was used.  $\text{CaCl}_2$  was a very unsatisfactory matrix. For the more volatile elements cathode excitation provided a higher sensitivity than anode excitation but with increased background and cyanogen emission.

The extraction of the elements Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb and Bi from hydrochloric acid into the three solvents cyclohexanone, cyclohexanol and cyclohexane was studied as a function of acid concentration. Cyclohexanone is a more efficient, but less selective extractant, than cyclohexanol. Cyclohexane has little extracting power for these elements.

Solvent extraction of hydrochloric acid solutions of a series of highly saline Antarctic lake waters into cyclohexanone was used to enrich the elements Zn, Pb, In, Bi, Fe, Mn, Mo prior to spectrographic analysis. For

(iii)

this, the percent extraction of Fe, Mn and Mo into cyclohexanone from 3N hydrochloric acid was obtained. This investigation has shown that one of these lakes, Lake Bonney, has most probably had a sea water origin. It is also possible that another of these lakes, Lake Fryxell, may also have contained sea water in the past. From the relative abundance of the various elements in the other lakes, it was possible to conduct a geochemical reconnaissance of the areas surrounding the lakes. This suggested that the two most likely areas for mineralisation in the McMurdo Oasis area of Antarctica are the region surrounding and feeding water to Lake Hoare and the region surrounding Lake Joyce.

A consideration of the theory of discontinuous countercurrent liquid-liquid extraction has shown that it is possible to simultaneously determine the extraction characteristics of a large number of elements for a given solvent system. If this technique is coupled with spectrographic analysis the determination is particularly rapid. The extraction of the elements Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, As, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, La, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb and Bi from hydrochloric acid into methyl isobutyl ketone was studied as a function of acid concentration. The data were obtained by studying spectrographically the distribution patterns of the elements after equilibration on a discontinuous countercurrent liquid-liquid extraction apparatus. A comparison

of some of the data so obtained with results for the same system as reported by other workers showed that the technique is valid and accurate.

Using these data it was possible to devise a scheme which could separate Fe from the majority of the trace elements extracted by cyclohexanone from a hydrochloric acid solution of a rock. By a combination of batch extraction with cyclohexanone and countercurrent distribution with methyl isobutyl ketone it was possible to obtain quantitative data for Zn and Ga and semiquantitative data for In in a wide range of silicate rocks by spectrochemical analysis. By the use of extraction into cyclohexanone coupled with atomic absorption spectrometry it was possible to determine the concentration of Pb, Cd and Bi in the same suite of rocks.

By the use of these techniques it was possible to obtain fresh abundance data for the above elements in the four standard rocks, G-1, W-1, CAAS syenite and CAAS sulphide.

The cyclohexanone/hydrochloric acid extraction system provides a satisfactory enrichment technique for the spectrographic analysis of trace elements in material with a low Fe content. For material containing a high concentration of Fe, it is necessary to combine this technique with discontinuous countercurrent liquid-liquid extraction to separate the Fe before spectrographic analysis.

However, under these conditions, certain elements can be determined by direct atomic absorption spectrometry of the cyclohexanone extract.



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