ACTA CHEMICA SCANDINAVICA 5 (1951) 1368–1374

Quantitative Spectral Analysis of Trace Elements in Water

SEPPO WILSKA

Department of Chemistry, Finland Institute of Technology, Helsinki, Finland

In a previous paper [1] we discussed the sensitivity of the porous cup electrode technique for direct spectral analysis of solutions, first described by Feldman [2]. The application of this technique (the PCE-technique) to the detection of trace elements in water is presented in this paper.

Trace elements in waters have been widely estimated by spectrographic methods, as well as by pure chemical, polarographic and flame photometric means. Most frequently the analysis has been carried out on the dry residue obtained by evaporation of the sample. The first spectrographic investigations of trace elements in water were made by Fresenius [3] in Germany (1934) and by Braidech and Emery [4] in USA (1935). Since then, many papers have been published describing similar work, and of these those by Strock [5] on trace elements in water at Saratoga Springs, by Lopez de Azcona [6] on Spanish mineral waters, and several by Kuroda [7,8,9] on Japanese mineral spring waters are of particular interest. Schleicher and Kaiser [10] used electrolysis combined with spectral analysis for the determination of the concentration of heavy metals in mine water. Dmitriev [11] proposed the excitation by an interrupted spark of filter paper impregnated with the solution to be investigated, the paper being moved after each spark interruption. The content of Al, Fe, Mn, Mg, and Cr in natural waters has been determined using this method. The "copper spark method", first described by Gerlach and Riedl [12] has been proposed for water analysis by Nachtrieb [13]. According to him, this method does not necessarily give high precision, but is very sensitive for the detection of most metallic elements. The method employing the evapouration of samples on graphite electrodes has been widely used, but no satisfactory method for the direct spectral analysis of water samples appears to have been presented in the literature.

Most of the errors which arise in the determination of trace elements in water are due to the introduction of impurities from the flasks, chemicals, air,

etc. or to the loss of material by adsorption or volatility, and these errors will become greater as the complexity of the method increases. A systematic study of these phenomena, like that made by Heller *et al.*[14] is desirable in all investigations made by indirect means. The author has attempted to find the simplest way of proceeding from the sample to the final analysis, even when a concentration must be made to obtain sufficient sensitivity.

EXPERIMENTAL

Water samples were collected in one-half liter bottles, paraffined inside and corked with natural cork stoppers. (Samples of 25 ml are, however, sufficient for complete analysis by this method.) The paraffined bottles do not contaminate the contents, nor do they adsorb the trace elements from water kept in them for periods even longer than one month. 15 Ml quartz test-tubes, with graduation marks at one and ten milliliters, were cleaned thoroughly. 10 Ml samples of water were placed in the test-tubes, which were then heated in a clean oven at a temperature not exceeding 100° C until the volume of the samples decreased to about 0.5 ml. This was usually done by keeping the samples in the oven overnight. The internal standard solution was then added and each tube was filled to the 1 ml mark with doubly quartz distilled water. In this way samples concentrated ten times were prepared for analysis. In some cases, especially when determining the concentrations of elements, for which the sensitivity of the method is high, or which are present in large amounts, it is desirable to take spectra from the original sample. In this case the internal standard solution is added directly to the 1 ml sample, and the increase in volume, caused by the internal standard solution, must be considered in the calculation.

The apparatus, electrodes, electrical and optical arrangements were the same as described previously[1]. It was observed, however, that more reproducible results were obtained by using a pre-spark period of 60 seconds (electrode filled), refilling the electrode, and then making an exposure of 180 seconds. The analytical gap was 4 mm. Kodak Scientific Plates III-O were used, and were developed in 1 : 2 diluted Kodak D-19b developer for 5 minutes at a temperature of 18° C, rinsed in a stop bath, fixed in a Kodak F-5 fixing bath, washed and dried in air.

Because foreign elements, present in large amounts, have a considerable effect to the appearance of the lines of trace elements, it is important to have standards resembling, as closely as possible, the samples to be analysed. The main mineral components in Finnish natural waters are calcium and magnesium, the former considerably exceeding the latter, and alkalies. Because

the content and ratios of alkalies are of interest, also, only calcium and magnesium were taken as base materials. Finnish natural waters usually are rather soft, the total hardness being on the average 50 ppm calculated as CaO. Consequently the standards used with the concentrated samples contained 400 ppm of calcium oxide and 100 ppm of magnesium oxide, corresponding to 40 and 10 ppm for the original samples. The Ca- and Mg-compounds used were purified according to the procedure described by Hughes [15] and no impurities could be observed in the treated salts. The standard substances were dissolved in 3 % nitric acid (purified by distillation), and dilutions were made and the internal standard was added in the usual way, the steps being 100, 30, —, 0.03, 0.01 ppm. As a result of a preliminary qualitative investigation of water samples, standards were made of the following elements: Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn. Spectra of standards were taken on each plate together with samples.

It was observed that the greatest variations in spectra were caused by different speeds of feeding the sample into the analytical gap. Hence it is unsatisfactory to use carbon lines as reference lines, as did Bretón [16], as the internal standard should be in the solution to be analysed. Feldman (*l. c.*) proposed the use of one of the lines of the hydroxyl band as the reference line, but it would be possible to use this line for only a few elements, and an internal standard must be added in any case.

According to Feldman (*l. c.*) only the wave length of the internal standard line need be considered, the excitation potential and volatility being of minor interest. This is undoubtedly true, as, although changes in the excitation conditions produce differences in the appearance of lines of elements which have different excitation potentials, these alterations do not appear without control, if a correct spark source is used. Continuous feeding overcomes the difficulties caused by different volatilities. An internal standard element should have a reasonable number of contamination-free lines covering a wide wavelength range so that one internal standard element only is needed, and it should not be present in the samples. None of the elements discussed in the literature as internal standards seemed to fulfill these requirements. Most of the rare elements, like Au and Ag, have only a few good lines. However, it was observed that platinum is an ideal internal standard element for this purpose. It has very distinct, contamination-free and self-reversal-free lines over the whole wavelength range from 2 300 to 3 068 A, and it has not been found in Finnish waters to date.

At a concentration of *ca.* 30 ppm of Pt, the following lines were found to be useful: Pt 2440.057 for Cu 2246.995, Cd 2265.017, Co 2286.156, Ni 2287.084, Ba 2304.235, and Fe 2395.625; Pt 2646.886 for Mn 2576.104, Pb 2833.069, and

Cr 2835.633; and Pt 3064.712 for Cu 3247.540, Zn 3345.020, Sr 3380.711, and Al 3082.155. A solution of pure Pt in aqua regia was made, and a suitable amount of this solution was added to the sample and standard to give a Pt-concentration of about 30 ppm.

The densities of the lines were measured with a Hilger non-recording microphotometer, and a plate calibration curve was made in the usual way using a step sector and iron-DC-arc. Intensity ratio-concentration working curves for each element were made using the lines mentioned above. No background correction was needed when determining Cu (using the line 2246.995), Co, Ni, Cd, Ba, and Fe. Background corrections for the other metals were made by subtracting the background intensity from the (line plus background) intensity. The working curves were straight lines.

Using the procedure suggested, the elements can be determined in the following minimum concentrations in the original water: Al 0.5, Ba 0.05, Cd 0.01, Co 0.05, Cu 0.01, Cr 0.05, Fe 0.05, Mn 0.001, Ni 0.5, Pb 0.5, Sr 0.07, Zn 0.6 ppm. When these values (multiplied by ten) are compared with the sensitivities given in a previous paper [1], obtained from pure solutions of elements, it is readily apparent that the presence of foreign elements, in this case Ca and Mg, has not had any appreciable effect upon the sensitivity.

PRECISION AND ACCURACY

To determine the precision obtainable, five separate and duplicate determinations were made using the same solution of each metal. Other metals were present in the same concentration, and Ca and Mg were used as the base mixture in the amounts described above. The time from the first to the last experiment was about five months. The results are given in Table 1. It can be seen that the average percentage deviation from the mean intensity ratio (analysis line/internal standard line) varies from 1.49 % (Cd) to 4.35 % (Mn). The standard percentage deviation, calculated as shown in the table, varies from 1.96 % (Cd) to 5.66 % (Cr). Considering all factors having an influence upon the reproducibility of determinations of this type, the results are considered to be quite satisfactory.

The accuracy has not been estimated by extensive comparison of the results with those obtained by independent methods. It is questionable if chemical methods can be considered more reliable than spectrographic methods when determinations are to be made in very dilute solutions, as considerable systematic errors may arise when standard analytical methods are employed. However, the nickel content of a mine water has been determined chemically by precipitation with dimethyl glyoxime, and the result obtained 20.0 ppm

Table 1. Precision obtained making five duplicate determinations of the concentrations of trace elements in the same solution during a time of five months.

Element and concentration ppm.		Mean intensity ratio anal. line/ref. line	Average deviation from the mean intensity ratio	Standard deviation * from the mean intensity ratio
Al	10	0.909	± 2.22 %	± 3.00 %
Ba	10	1.091	4.02	5.17
Cd	10	1.470	1.49	1.96
Co	1	0.601	2.40	2.40
Cu	100	1.579	3.14	3.80
Cr	1	1.336	3.66	5.66
Fe	33	4.700	1.66	2.02
Mn	1	2.040	4.35	5.45
Ni	33	1.012	1.80	2.24
Pb	10	1.204	3.66	4.72
Sr	1	0.710	2.86	4.95
Zn	33	0.939	3.32	4.42

* Standard deviation: $s = \pm \sqrt{\frac{\Sigma d^2}{n-1}}$ if d is the percentage deviation and n the number of determinations, in this case 10.

is close to the 21.0 ppm obtained by spectrographic means, the deviation being in this case 5 %. It seems very likely that the precision of this method can be regarded as the same as the accuracy. The most common source of errors is that introduced by the use of synthetic standards, but this seems to be negligible in this procedure, as it is possible to make the standard solution very similar to the sample. Moreover, moderate changes in the concentration of basic elements do not have an appreciable influence on the working curves for different elements.

Further details and results concerning the concentrations of trace elements in Finnish ground waters and mine waters will be presented in a forthcoming communication [17].

OTHER APPLICATIONS

Undoubtedly, this procedure can be applied to liquids such as soil extracts, biological fluids etc, and in the last mentioned case especially the small amount of sample required for the complete analysis is most advantageous. Major elements as well as trace elements may be determined by this method, a step sector being used if necessary. In this case, however, because an intermittent light source is used, a special study of the working conditions should be made, as pointed out by Gillis and Eeckhout [18].

The relatively high precision obtainable by this procedure has prompted author to apply the PCE-technique to the determination of adsorption isotherms in very dilute solutions. A preliminary investigation has been made, and it has been observed that the sensitivity of the beryllium determination could be extended to 0.001 ppm without concentrating the samples. The adsorption isotherms of beryllium on glass were determined in solutions containing 0.003, 0.01 and 0.03 ppm of Be. Samples of 1 ml were taken at different time intervals, and the decrease in Be-concentration was determined spectroscopically. The advantage of the use of small samples is evident: they have no significant influence on the total volume and they can be removed quickly. Further the use of spectroscopical methods makes it possible to analyse a large number of samples in a relatively short time and to determine the concentrations of elements, the chemical analysis of which would be difficult and time-consuming. Preliminary results using this technique for adsorption studies have been quite satisfactory.

SUMMARY

The application of the PCE-technique of direct spectral analysis of solutions to the determination of trace elements in water is described. Using samples of about 25 ml each, it is possible to make a duplicate determination of different elements in the following minimum concentrations: Al 0.5, Ba 0.05, Cd 0.01, Co 0.05, Cu 0.01, Cr 0.05, Fe 0.05, Mn 0.001, Ni 0.5, Pb 0.5, Sr 0.07, Zn 0.6 ppm. The concentration of the sample is carried out in a very simple manner to avoid contamination from air and flasks, and errors due to adsorption. A precision of 1.49 %—4.35 % average deviation and 1.96 %—5.66 % standard deviation from the mean intensity ratio of lines is obtained. A preliminary report is given on the application of this method to the determination of adsorption isotherms.

REFERENCES

1. Wilska, S. *Acta Chem. Scand.* **5** (1951) 890.
2. Feldman, C. *Anal Chem.* **21** (1949) 1041.
3. Fresenius, L. *Z. deut. geol. Ges.* **85** (1934) 540.
4. Braidech, M. M., Emery, F. H. *J. Am. Water Works Assoc.* **27** (1935) 557.
5. Strock, L. W. *Am. J. Sci.* **239** (1941) 857.
6. Lopez de Azcona, J. M. *Notas y comun. inst. geol. y minero España No.* **17** (1947).
7. Kuroda, K. *Bull. chem. Soc. Japan* **14** (1939) 303.
8. Kuroda, K. *Ibid.* **17** (1942) 213, *C. A.* **41** (1947) 4594.
9. Kuroda, K. *Mitt. deut. Ges. Natur- u. Völkerkunde Ostasiens* **33** (1942) Cl, *C. A.* **43** (1949) 4793.

10. Schleicher, A., Kaiser, N. *Z. Anal. Chem.* **105** (1936) 393.
11. Dmitriev, K. G. *Zavodskaya Lab.* **15** (1949) 63, *C. A.* **43** (1949) 5325.
12. Gerlach, W., Riedl, E. *Z. anorg. Chem.* **221** (1934) 103.
13. Nachtrieb, N. H. *Principles and practice of spectrochemical analysis*, New York (1950) p. 277.
14. Heller, K., Kuhla, G., Machek, F. *Mikrochemie* **23** (1937) 78.
15. Hughes, R. C. *J. optical Soc. Am.* **33** (1943) 49.
16. Bretón, A. S. *Anales real soc. españ. fís. quím., Ser. A* **46** (1950) 283.
17. Wilska, S. *Trace elements in Finnish ground and mine waters.* Dissertation (Manuscript).
18. Gillis, J., Eeckhout, J. *Mededeel. Koninkl. Vlaam. Acad. Wetenschap, Belg., Klasse Wetenschap* **11** (1949) No. 9, 10; No. 12, 5.

Received August 27, 1951.