Determination of copper in geological material by neutron activation and γγ-coincidence

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Résumé—La fluorescence violette du plomb à 480 mμ en solution acide chlorhydrique concentré-chlorure de potassium (maximum d'excitation à 270 mμ) fournit une méthode de dosage spectro-fluorimétrique de 10–60 μg de plomb. On a établi les conditions optimales du dosage, et examiné les effets de 31 ions étrangers à des teneurs molaires 50 fois en excès. L'interférence du fer(III) et du vanadium(V) est éliminée par addition de chlorure d'étain(II) et celle du chrome(VI) par traitement au sulfite de sodium.

REFERENCES

1. P. Pringsheim and H. Vogels, *Physica*, 1940, **1**, 225.
2. G. F. Kirkbright, T. S. West and C. Woodward, *Talanta*, 1965, **12**, 517.
3. H. Goto, *Sci. Rep. Tohoku. Imp. Univ., First Ser.*, 1940, **29**, 204.
4. N. Strafford, P. F. Wyatt and F. G. Kershaw, *Analyst*, 1945, **70**, 232.
5. C. Merritt Jr., H. M. Hershenson and L. B. Rogers, *Anal. Chem.*, 1953, **25**, 572.

Determination of copper in geological material by neutron activation and gamma–gamma coincidence spectrometry

THE feasibility of determining copper by activation analysis is dependent on the distribution of other elements, capable of activation, in the samples of interest. In most cases copper is present as a minor or trace element, and hence the activity of ^{64}Cu or ^{66}Cu produced by neutron activation will be shielded by activities originating from other elements present. In geological samples the most serious complication derives from ^{24}Na, formed by activation of sodium, which is usually present at the per cent level.

Thoresen,[1] using computer techniques for the analysis of gamma-spectra from soil samples, found a practical limit of detection for copper corresponding to a Na/Cu ratio of about 10^4. Schmitt et al.[2] determined amounts of copper of 30–170 ppm in meteorites with a sodium content of 0·2–0·6%, using the peak area ratio 0·51 MeV/2·75 MeV in the gamma-spectrum of a ^{24}Na-standard to correct for the contribution of ^{24}Na to the 0·51-MeV annihilation peak of ^{64}Cu in the gamma spectra of the meteorite samples.

Application of a Ge(Li) detector has been reported in the case of a sulphide ore,[3] where the ^{24}Na content was too low to cause any serious interference.

The fact that ^{64}Cu is one of the very few positron-emitting nuclides produced by thermal neutron activation has led several investigators to take advantage of the 180° annihilation quanta for gamma-gamma coincidence measurements. In this manner the detection rate of ^{64}Cu as compared to most other activities is greatly enhanced. The use of this principle for the determination of copper by neutron activation was first mentioned by Ljunggren,[1] who proposed applications to biological materials. More recent investigations have included determinations of amounts of copper in beryllium,[5] iron,[6] and bismuth[7] in the ppm range. Gorski et al.[8] employed a similar technique for the determination of copper in ores, using 14-MeV neutrons and measuring the activity of the 9·8 min positron emitter ^{62}Cu, produced by $(n, 2n)$ reactions. This technique, however, does not seem to be applicable to samples containing only trace amounts of copper, as some of the major elements in rocks also form β^+-emitters by 14-MeV neutron activation.

The gamma–gamma coincidence technique should be suitable for increasing the sensitivity of copper determinations in the presence of a large excess of ^{24}Na, since the annihilation of all β^+-particles from ^{64}Cu can be made to occur close to the sample position, and hence can be detected with a reasonable probability by coincidence detectors placed in opposite directions, while the pair production process of ^{24}Na is most likely to take place somewhere else in the system, thus giving a very minute probability of 180° coincidence detection. In the present work applications of such a technique for the copper determination in some geological samples are shown.

EXPERIMENTAL

Instrumentation

The detectors used for the measurements were Harshaw integral line detectors with 2 × 2 in. NaI(Tl) crystals directly attached to RCA 6342 A photomultiplier tubes. The detectors were connected

to Hamner charge-sensitive preamplifiers and linear amplifiers capable of delivering either a symmetrical double-delay line or a single-delay line output pulse. From the linear amplifiers the pulses were fed to Hamner jitter-free pulse-height analysers which were coupled to a fast coincidence unit with a variable resolving time in the range 10–150 nsec. The timing of each single channel pulse analyser was adjustable over a range of 200 nsec, and accidental coincidence rates were evaluated by introducing a fixed delay of 0·5 μsec in one channel. The output of the coincidence unit was used to gate a Tullamore transistorized 400-channel pulse-height analyser which was used for pulse analyses of the spectrum from one detector. The spectrum recorded by the analyser could be printed out on a Monroe data printer.

Samples and standards

The samples selected for this investigation were five different qualities of iron ore (I–V) and two samples of silicate rocks, *i.e.*, an amphibolite (VI) and a diabase (W-1). The standard rock W-1, issued by the U.S. Geological Survey, was included to check the accuracy of the method.

The standard rock "Sulphide ore-1" from the Canadian Association for Applied Spectroscopy was selected as standard. This rock has a copper content of 8300 ppm,[9] and a sodium content of 0·70%. The value 8300 ppm, which is the mean value of analyses mainly based on chemical and emission spectrographic techniques, was checked with radiochemical activation analysis according to the method of Brunfelt *et al.*[10] and agreement was found within experimental error. To correct for the contribution of [24]Na in the measurements, it was also necessary to have a sodium standard. The standard rock STM-1 from the U.S. Geological Survey, with a sodium content[11] of 6·1% and a copper content[10] as low as 2·0 ppm was chosen for this purpose.

Procedure

Finely crushed samples (about 300 mg) were transferred to small polyethylene vials and irradiated for 30 min at a thermal neutron flux of $2·5 \times 10^{12}$ n.cm^{-2}.sec^{-1} in the JEEP-I reactor (Kjeller, Norway). After the activation the samples were allowed to stand for 24 hr, for the decay of the [56]Mn activity. Portions of 50–100 mg of the irradiated samples were then weighed into flat-bottomed polyethylene tubes of 6·0 mm inner diameter. For STM-1 a sample size of 20 mg was used, otherwise the [24]Na activity induced would have been too strong.

For the gamma-activity measurements the tubes were mounted in a perspex sample holder placed in the central axis of the detectors, which were kept at an angle of 180° relative to each other. The distance between the sample and the detectors was so adjusted that the dead time of the analyser in no case exceeded 40% when the detector pulses were fed *via* the preamplifier directly into the multichannel analyser.

In the coincidence measurements a counting period of 5–20 min was employed, depending on the amount of copper in the sample. The total gamma-spectra of the samples were also recorded to measure the sodium content of the samples through the 1·37-MeV photopeak of [24]Na. By means of these sodium values and of the coincidence counting rate of the sodium standard STM-1, correction could be made for the [24]Na contribution of the 0·511-MeV peak in the gamma-gamma coincidence measurements.

The sodium content of the copper standard corresponded to a correction of 0·25%. On the other hand, the copper content of the sodium standard contributed to 1·0% of the 0·511-MeV coincidence peak. The areas of the photopeaks were evaluated according to the method of Covell.[12]

In Fig. 1 the effect of applying the coincidence principle as compared to a direct measurement is illustrated for sample IV in Table I.

RESULTS AND DISCUSSION

The results obtained for each of the seven samples, together with the mean values, are given in Table I. The relative standard deviation of a single value has been calculated for each sample, and is in the range 1·9–6·4%. In the table data are also included demonstrating the effect of the [24]Na interference at various Na/Cu abundance ratios.

To get an estimate of the reliability of the method for samples with a high Na/Cu ratio, sample VI was analysed by radiochemical activation, using the method of Brunfelt *et al.* The results of this investigation are given in Table II, and show very good agreement with the gamma-gamma coincidence results. The present result for W-1 is also in agreement with the previous neutron-activation values quoted in the table. Good agreement is also found with the recommended value of 110 ppm given by Fleischer.[17] This value is based on emission spectrographic and colorimetric data.

The spread of replicate determinations in this work is due to counting errors and errors due to neutron flux inhomogeneity in the irradiation position. Neutron-shielding effects are not expected to affect the present results seriously, since no strong neutron-absorbing elements are present in
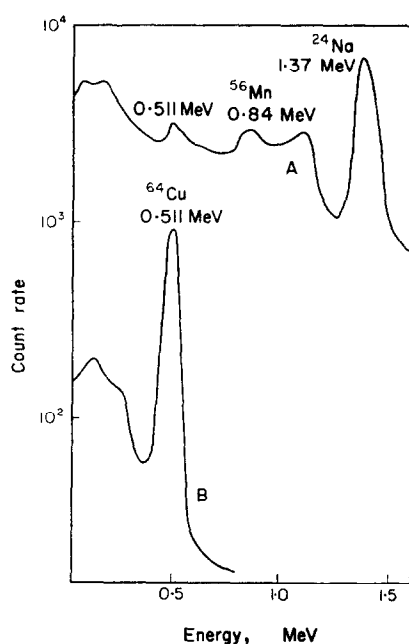
FIG. 1.—Single and coincidence gamma-spectra of sample IV (Table I) recorded one day after irradiation.
A: Single spectrum—2-min counting time
B: Coincidence spectrum—10-min counting time

TABLE I.—COPPER CONTENT OF SOME GEOLOGICAL SAMPLES DETERMINED BY NEUTRON ACTIVATION AND GAMMA–GAMMA COINCIDENCE SPECTROMETRY

Sample	I	II	III	IV	V	VI	W-1
Cu-content ppm	665	371	317	250	224	61	116
	634	384	307	284	231	57	118
	636	376	314	242	213	63	116
	661	389	315	243	218	57	112
	632	381	301	255	204	56	115
Mean, ppm	646	380	311	255	218	59	115
Relative standard deviation of single value, %	2·5	1·9	2·1	6·4	4·7	5·2	2·0
Na-content, %	0·213	0·170	0·260	0·70	0·84	1·95	1·50
Na/Cu	3·3	4·5	8·4	27	39	330	130
Fraction of 0·511-MeV photopeak due to ^{24}Na %	1·0	1·4	2·5	7·5	11·0	49	26·5

appreciable amounts in the samples. Possible interference from the nuclear reaction $^{64}Zn(n, p)^{64}Cu$ might be significant, but becomes important only if the zinc content is 100 times higher than the copper content. As no serious systematic errors seem to influence the results, and as the agreement with results obtained by other techniques is good, the error of the present method is probably of the order of ±5%, even for the silicate rock samples.

TABLE II.—COMPARISON OF THE GAMMA–GAMMA COINCIDENCE DATA FOR Cu IN SAMPLES VI AND
W-1 WITH RESULTS OBTAINED BY OTHER METHODS

Sample	Present work		Previous values	
	Gamma–gamma coincidence	Radiochemical	Neutron activation (reference)	Recommended value
VI	59	56, 57, 59, 54 mean 57	—	—
W-1	115	—	116 (10) 112 (13) 120 (14) 110 (15) 116 (16)	110

CONCLUSION

The present neutron activation method based on gamma-gamma coincidence measurements should facilitate rapid and accurate measurements of copper in the concentration region 0·01–0·1%. In this region the conventional type of instrumental activation analysis usually becomes difficult owing to the contribution from ^{24}Na to the gamma-spectrum. It is also possible to get good results at lower copper concentrations, but long counting periods are necessary to obtain satisfactory counting statistics. For sodium-rich rocks with copper contents at the ppm level, methods based on rapid radiochemical separation would therefore be preferable.

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Summary—The copper content of some geological samples has been determined by thermal neutron activation and subsequent coincidence gamma-spectrometry, taking advantage of the 180° annihilation quanta of ^{64}Cu. By this means the interference of ^{24}Na, which is often the major gamma-activity induced in geological materials, is greatly reduced. The method is precise to about ±5%, and the error is of the same order. The method should be especially attractive for application to samples with a copper content of 100–1000 ppm.

Zusammenfassung—Der Kupfergehalt einiger geologischer Proben wurde durch Aktivierung mit thermischen Neutronen und anschlie-ßende Koinzidenz-Gammaspektometrie bestimmt, wobei die 180°-Vernichtungsquanten von ^{64}Cu ausgenutzt wurden. Auf diese Weise wird die Störung durch ^{24}Na, das oft den Großteil der in geologischem Material induzierten Gamma-Aktivität darstellt, stark reduziert. Die Methode ist auf etwa ±5% genau, der Fehler liegt in der gleichen Größenordnung. Die Methode sollte besonders zur Anwendung auf Proben mit Kupfergehalten von 100–1000 ppm vorteilhaft sein.

Résumé—On a déterminé la teneur en cuivre de quelques échantillons géologiques par activation de neutrons thermique suivie de spectrométrie de coïncidence gamma, tirant avantage de l'annihilation 180° des quanta de ⁶⁴Cu. De cette manière, l'interférence de ²⁴Na, qui est souvent la principale activité gamma induite dans les matériaux géologiques, est fortement réduite. La méthode est précise à environ ±5% et l'erreur est du même ordre. La méthode devrait être particulièrement intéressante pour son application à des échantillons à teneur en cuivre de 100–1000 p.p.m.

REFERENCES

1. P. Thoresen, *Acta Chem. Scand*, 1964, **18**, 1054.
2. R. A. Schmitt, R. H. Smith and G. G. Goles, *J. Geophys. Res*, 1965, **70**, 2419.
3. J. F. Lamb, S. G. Prussin, J. A. Harris and J. M. Hollander, *Anal. Chem*, 1966 **38**, 813.
4. K. Ljunggren, *Pure Appl. Chem*, 1960, **1**, 31.
5. J. Petit and C. Engelmann, *IAEA Seminar on the Practical Application of Short-Lived Radioisotopes*, paper SM-32/28 (1962).
6. R. Malvano and P. Grosso, *Anal. Chim. Acta*, 1966, **34**, 253.
7. J. I. Kim, A. Specke and J. Hoste, *ibid*, 1965, **33**, 123.
8. L. Gorski, *Talanta*, 1964, **11**, 1135.
9. G. R. Webber, *Geochim. Cosmochim. Acta*, 1965 **29**, 229.
10. A. O. Brunfelt, O. Johansen and E. Steinnes, *Anal. Chim. Acta*, 1967, **37**, 172.
11. A. O. Brunfelt, and E. Steinnes, *Geochim. Cosmochim. Acta*, 1966, **30**, 921.
12. D. F. Covell, *Anal. Chem*, 1959, **31**, 1785.
13. A. A. Smales, D. Mapper and A. J. Wood, *Analyst*, 1957, **82**, 75.
14. H. Hamaguchi, *Geochim. Cosmochim. Acta*, 1965, **29**, 821.
15. O. T. Høgdahl, *Progress Report II*, University of Michigan, 1962, p. 62.
16. L. Greenland, and J. F. Lovering, *Geochim. Cosmochim. Acta*, 1963, **27**, 897.
17. M. Fleischer, *ibid.*, 1965, **29**, 1263.

Kinetic titration with differential thermometric determination of the end-point

THERMOMETRIC end-point determination has been used so far in the titration of solutions with minimum concentrations of 10^{-3}–$10^{-4}M$. The temperature changes occurring in the titration of solutions more dilute than this cannot be separated with sufficient clarity from the background changes stemming from various sources (heat conduction, evaporation, temperature differences inside the system, heat of dilution, heat of dissociation, *etc.*). In the past few years we have been able to lower this concentration limit by the introduction of catalytic reactions,[1,2] and now describe a differential thermometric method of end-point detection.

The velocity of homogeneous catalytic reactions is proportional to the concentration of the catalyst and to some function of the concentrations of the other reacting substances. In two solutions identical except that catalyst is absent from one of them (reference solution), the reaction velocities can be made identical if the reference solution is titrated with a dilute ($10^{-3}M$) solution of catalyst until the catalyst concentration in both solutions becomes the same. The titration can be monitored by measuring the difference in the rates of change of temperature in the two solutions by means of thermistors in a Wheatstone bridge circuit; the rates becoming equal at the end-point. If an excess of titrant has been added the end-point may be established by back-titration of the sample solution with catalyst.

If the temperature change is not too great, its rate will be related to the rate of reaction through the heat of reaction:

$$dT/dt = k \cdot dc/dt \tag{1}$$