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Determination of Chromium in Rocks by Neutron Activation and Anion Exchange

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DETERMINATION OF CHROMIUM in rocks has so far most frequently been carried out by emission spectrographic techniques. This element can also be determined with a high sensitivity by neutron activation. Applications of this technique to geochemical samples have been reported by Bate *et al.* (1) and by Turekian and Carr (2). Most of the radiochemical separation methods published have been based on the precipitation of BaCrO_4 as a final step and determination of chemical yield by weighing, which results in a considerable working time for each sample. In the present paper a method based on anion exchange separation and determination of chemical yield by reactivation is described. By this means it is possible for one analyst to process a great number of samples simultaneously. The method has been applied to a series of standard rocks, which are listed in Table I.

EXPERIMENTAL

Apparatus. An Inter technique 400-channel gamma-spectrometer SA-40 was used, with a 3×3 -inch NaI(Tl) crystal. The ion exchange columns used had 9-mm i.d. and measured about 15 cm high.

Reagents. The purity of all reagents was *Pro analysi*. Chromium standard solution was prepared by dissolving 50 mg of the metal in a small volume of hydrochloric acid and diluting with water to a concentration of 0.5 mg/ml. Chromium carrier solution was an aqueous solution containing 30 mg/ml of chromium as potassium chromate. Ascorbic acid solution was prepared by dissolving 45 grams of L(+)-ascorbic acid in 500 ml of 1N hydrochloric acid. The anion exchange resin used was Dowex 1-X8, 100–200 mesh. Height of the resin bed was 4 cm.

Irradiation. Accurately weighed rock samples of about 100 mg were wrapped in aluminum foil and irradiated for 7 days in the JEEP-I reactor (Kjeller, Norway) at a thermal neutron flux of about 1.5×10^{12} neutrons/cm² second. About 0.6 ml of chromium standard solution was sealed in a silica ampoule and irradiated together with the samples.

Procedure. The irradiated sample was transferred to a nickel crucible containing 1.00 ml of chromium carrier evaporated to dryness and 2 grams of sodium hydroxide, and fused for 5 minutes. After cooling, the resulting fusion cake was dissolved in 25 ml of water and centrifuged. The supernatant liquid was acidified with nitric acid and poured through a filter on the top of an anion exchange column preequilibrated with 1N nitric acid. The resin bed was

Table I. Chromium Content of Standard Rocks

Rock	Supplier	Chromium, ppm
Andesite AGV-1	U. S. Geological Survey	9.6 \pm 0.3
Basalt BCR-1	U. S. Geological Survey	13.3 \pm 0.8
Diabase W-1	U. S. Geological Survey	114 \pm 3
Granite G-2	U. S. Geological Survey	7.5 \pm 0.1
Granodiorite GSP-1	U. S. Geological Survey	11.4 \pm 0.6
Nepheline Syenite STM-1	U. S. Geological Survey	1.4 \pm 0.1
Tonalite T-1	Geological Survey of Tanganyika	17.2 \pm 0.8
Sulfide ore-1	Canadian Association of Applied Spectroscopy	406 \pm 4
Syenite rock-1	Canadian Association of Applied Spectroscopy	49 \pm 2

washed with 2×5 ml of 1N nitric acid, 2×5 ml of water and 2×5 ml of 6N hydrochloric acid. The still-retained Cr was then reduced to Cr(III) and eluted with 4×5 ml of ascorbic acid solution. The eluate was collected in a 100-ml polyethylene bottle for gamma-activity measurements.

By means of a micropipet, two 250- μ l portions of the standard solution were withdrawn from the broken silica ampoule and transferred to polyethylene bottles. The volumes were made up to 20 ml with dilute nitric acid. The chemical yield is usually 60–70%.

Activity Measurements. The samples were counted for 10–30 minutes, depending on the activity level. The measurements were based on the 0.32-MeV gamma peak of 27.8-day ^{51}Cr , formed by (n, γ) reaction, and the area under the peak was evaluated according to the method of Covell (3). No impurities could be detected in the gamma spectra, except in the case of Syenite rock-1. This standard rock has a thorium content of about 1500 ppm (4), giving rise to a considerable activity of ^{233}Pa , with a half-life very similar to ^{51}Cr and a principal gamma-ray of about the same energy. However, ^{233}Pa also has a peak at 0.103 MeV, in a region where the ^{51}Cr spectrum is smoothshaped. By means of a pure ^{233}Pa source, it is easy to correct for possible contamination, either by spectrum stripping or by simple calculation. The activity of ^{233}Pa in the Syenite rock-1 samples amounted to 15–20% of the 0.32-MeV peak area, corresponding to a decontamination factor of about 10^4 for ^{233}Pa .

(1) G. L. Bate, H. A. Potratz, and J. R. Huizenga, *Geochim. Cosmochim. Acta*, **18**, 101 (1960).

(2) K. K. Turekian and M. H. Carr, *Ibid.*, **24**, 1 (1961).

(3) D. F. Covell, *ANAL. CHEM.*, **31**, 1785 (1959).

(4) G. R. Webber, *Geochim. Cosmochim. Acta*, **29**, 229 (1965).

Determination of Chemical Yield. After the gamma-activity measurements had been completed, the samples were diluted to 100 ml with water. About 1.2 ml of each solution was sealed in a polyethylene ampoule and irradiated for 3 hours together with aliquots of the carrier solution treated in a similar way. After 2 days' delay the induced activity of ^{51}Cr in each solution was measured as described above. In the case of Sulfide ore-1, which had the highest ^{51}Cr activity, it was necessary to correct for the remaining activity from the first irradiation by gamma-counting 1.00 ml of the diluted sample and subtracting. For the other samples this correction was unnecessary.

RESULTS AND DISCUSSION

The mean values listed in Table I for the chromium content of the standard rock are for two determinations per sample. As an approximate measure of the precision of the method, the mean relative standard deviation has been calculated to be $\pm 3\%$.

The present value 114 ± 3 ppm for W-1 is in excellent agreement with the previous neutron activation results, 113 ppm by Turekian and Carr (2) and 116.3 ppm by Das and Pendharkar (5). The agreement with the 120-ppm value recommended in the review report by Ahrens and Fleischer (6) is also satisfactory.

- (5) M. S. Das and M. S. Pendharkar, unpublished work (1964), cited in M. Fleischer, *Geochim. Cosmochim. Acta*, **29**, 1263 (1965).
 (6) L. H. Ahrens and M. Fleischer, *U. S. Geol. Surv. Bull.*, **1113**, 83 (1960).

Most errors of importance in the present method, errors due to neutron flux gradients in the irradiation container and counting errors, are random errors, and will be included in the observed spread of duplicate determinations. Possible systematic errors are most likely to occur from neutron shielding effects or from interfering nuclear reactions. Because a dilute solution was used as standard, and none of the major elements in the standard rocks are strong neutron absorbers, the shielding effects were negligible. The only significant interfering reaction is $^{54}\text{Fe}(n, \alpha)^{51}\text{Cr}$, but its contribution is only of the order 0.1–0.2% and no correction was therefore deemed necessary. The mean values presented, on the basis of the preceding discussion, are probably accurate to $\pm 5\%$.

If an additional precipitation step had been added in the chemical procedure, the size of the final sample would have allowed the counting to be performed in the well of the NaI crystal. This would increase the sensitivity of the method by about a factor of 10. Such a step would mean a considerable increase in the amount of work. As the observed precision was satisfactory and the content of chromium in most minerals and rocks is above 1 ppm, no such additional step was introduced. The method in its present form should be satisfactory for the determination of Cr in most geochemical samples.

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Specific Surface Area by Low-Pressure Permeametry

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PERMEAMETRY IS A WELL KNOWN TECHNIQUE (1–3) for evaluating the relative size parameters of powders. A gas, usually air, is made to flow laminarily through a chamber containing the granular material at essentially atmospheric pressure, while the flow rate and accompanying pressure drop across the chamber are measured. The results agree approximately with microscopic or screening analyses when the particles are relatively coarse and spherical; they may be misleading when the particles are irregular and fine.

That this should be so is apparent from an examination of the flow pattern. A gas near atmospheric pressure under a low driving force moves in viscous flow through a channel when the diameter of the space is much greater than the mean free path of the gas molecules. The velocity is actually zero at the boundary, most of the flow occurring along the center of the open spaces among the particles. Roughness on a microscopic scale thus has little effect on the resistance to flow. Knudsen flow prevails when the mean free path of the gas molecules is approximately 10 times the diameter of the passageway (4). In this case the flow is governed not by the

gas viscosity but by collisions of the gas molecules with the confining surfaces.

The present work describes a flow apparatus and a technique of operation at progressively lower pressures; the technique achieves specific surface area results that are in remarkably close agreement with low temperature gas adsorption (BET) values for the same material. The analysis (5) is based on the equation

$$s_w = \frac{24}{13} \sqrt{\frac{2}{\pi}} \frac{\epsilon^2}{\rho Q \sqrt{MRT}} \frac{\Delta P}{L} \quad (1)$$

derived (6) in part by applying a statistical treatment to describe the motion of a free molecule passing through a random pore space. Nomenclature is defined at the end of the article.

EXPERIMENTAL

A schematic diagram of the apparatus is given in Figure 1. It consists of a sample holder, a 0- to 20-mm Hg differential pressure gauge, a micrometer flow-regulating valve, a pressure-indicating manometer, a flow-rate indicator, a mechanical

- (1) P. C. Carman, *J. Soc. Chem. Ind. (London)*, **57**, 825–34 (1938).
 (2) R. D. Cadle, "Particle Size," Reinhold, New York, 1965, pp. 132–4.
 (3) C. Orr, Jr., and J. M. DallaValle, "Fine Particle Measurement," Macmillan, New York, 1959, pp. 134–63.
 (4) G. N. Patterson, "Molecular Flow of Gases," Wiley, New York, 1956, pp. 159–63.

- (5) B. V. Deryagin, N. N. Zakhavaeva, M. V. Talaev, B. N. Parfanovich, and E. V. Makarova, "Research in Surface Forces," Consultants Bureau, New York, 1964, pp. 155–60.
 (6) B. V. Deryagin, *Akad. Nauk SSSR*, **53**, 623–6 (1946).