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The Determination of Copper, Nickel and Cobalt in Rocks by Atomic Absorption Spectrometry Using a Cold Leach

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PRELIMINARY REMARKS

THE METHOD DESCRIBED IN THIS PAPER is an application of
the studies carried out by N. P. Smirnova et al. (1968),
wherein certain trace elements occurring in rocks as sul-
phide minerals were preferentially dissolved by the action
of hydrogen peroxide in the presence of ascorbic acid. The
ascorbic acid lowers the pH of the solution to approxi-
mately 2.5 and provides a reducing medium which inhibits
the oxidation of ferrous sulphate to ferric sulphate, which
in turn hydrolizes to hydrous ferric oxide. The ascorbic
acid - hydrogen peroxide solution prepared as described
below was found to decompose galena, arsenopyrite, chal-
copyrite, pyrite, pyrrhotite, pentlandite, tetrahedrite, sphale-
rite and awaruite.

Mixed standard solutions for the calibration of the
atomic absorption spectrophotometer were initially pre-
pared in the same concentration of ascorbic acid - hy-
drogen peroxide as was used for the decomposition of the
samples. These standard solutions were found to be un-
stable over periods longer than three or four days. A fresh
set of standard solutions contained in ascorbic acid and hy-
drogen peroxide were compared against a set of standard
solutions contained in 1N HNO_3. There was no appreciable
difference in the per cent absorbance readings between the
standard solutions prepared in the two media (Table I).

Standard solutions contained in 1N HNO_3 have been
found to be stable for over a year, and these are used for
calibration.

TABLE I — Comparison of Standard Solutions Prepared in Ascorbic Acid - Hydrogen Peroxide and in 1N HNO_3

Concentration µg/ml	Cu, % Absorption		Ni, % Absorption		Co, % Absorption	
	H_2O_2 – Ascorbic Acid	1N HNO_3	H_2O_2 – Ascorbic Acid	1N HNO_3	H_2O_2 – Ascorbic Acid	1N HNO_3
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.5	18.5	18.5	7.0	7.1	11.8	11.6
1.0	36.6	36.9	13.8	13.8	23.0	23.2
2.0	70.4	70.0	24.2	24.2	43.5	43.9
4.0	—	—	44.7	44.9	79.7	80.1

ANALYTICAL PROCEDURE

Decomposition of the Sample

1. Into a clean dry test tube (16 by 125 mm), calibrated at 10 ml, weigh a 100-mg sample of the ground rock. A larger sample weight may be used if low values are anticipated.
2. Add 7 ml of ascorbic acid - hydrogen peroxide mixture and allow to stand approximately 18 hours (overnight), with occasional mixing. Do not heat.
3. Dilute to the 10-ml mark with metal-free water. Stopper the test tube with a clean cork and shake vigorously to mix.
4. Centrifuge for 5 minutes to obtain a clear supernatant solution.

General Procedure for Calibration of Instrument

1. The operating parameters described here refer to the Perkin Elmer Model 303 atomic absorption spectrophotometer. Other makes of intruments will require changes in some of these parameters.

Parameter	Copper	Nickel	Cobalt
Meter Response	1*	1*	1*
Filter	out	out	out
Scale	x5	x2	x5
Slit	4 (7Å)	3(2Å)	3(2Å)
Source Current	15 ma	25 ma	30 ma
Range	U.V.	U.V.	U.V.
Wavelength	3,247 Å	2,320 A	2,407 A
Burner	10 cm single slot	Boling	Boling
Air Pressure	30 psi	30 psi	30 psi
Air Flow	9*	9*	9*
Acetylene Pressure	8 psi	8 psi	8 psi
Acetylene Flow	8*	7½*	7½*

*Arbitrary units given by Perkin-Elmer

2. Aspirate 1N HNO_3 into the flame and zero the instrument.
3. Using the parameters listed above, the following standard solutions are used for calibration:

   Cu: 0.5, 1.0 and 2.0 $\mu g/ml$
   Ni: 0.5, 1.0, 2.0, 4.0, 6.0 and 8.0 $\mu g/ml$
   Co: 0.5, 1.0, 2.0 and 4.0 $\mu g/ml$

4. Calibration curves are plotted relating per cent absorption and $\mu g/ml$.

General Procedure for Analysis of Samples

1. After calibrating, aspirate 1N HNO_3 and readjust zero if necessary.
2. Aspirate sample solutions and record per cent absorp-tion. Care should be taken not to suck any of the sediment into the burner. Aspirate 1N HNO_3 between each sample and check a calibration standard after every tenth sample. If check standard changes by more than 1 per cent absorption, recalibrate and repeat the previous ten samples.
3. Using calibration curves, interpolate per cent absorption of samples to obtain $\mu g/ml$. Calculate the concentration in parts per million using the equation:

$$\text{ppm element} = \frac{\mu g/ml \times 10}{\text{sample weight (gm)}}$$

4. Should the sample be above the top standard of the calibration curve, an aliquot of the sample solution may be diluted to 10 ml with the appropriate volume of ascorbic acid - hydrogen peroxide mixture and metal-free water. Alternatively, the sensitivity of the instrument may be lowered by reducing the scale expansion and/or using a smaller burner. This permits the use of standards up to considerably higher concentrations.

Preparation of Reagents

1. *1 per cent acid solution*: Dissolve 5.0 gm ascorbic acid in metal-free water and dilute to 500 ml with metal-free water. This solution should be prepared freshly just prior to using.
2. *Ascorbic acid - hydrogen peroxide mixture*: Add 200 ml of 30 per cent hydrogen peroxide to 500 ml of ascorbic acid and mix thoroughly. This solution is made up freshly each day.
3. *Mixed copper, nickel and cobalt standard solution*: 1000 $\mu g/ml$ (*Solution A*). In a 1000-ml volumetric flask, dissolve 3.9297 gm of copper sulphate ($CuSO_4.5H_2O$), 4.0487 gm of nickelous chloride ($NiCl_2.6H_2O$) and 4.0372 gm of cobaltous chloride ($CoCl_2.6H_2O$) in about 900 ml of metal-free water. Add 6 ml of concentrated nitric acid mix and allow to cool to room temperature. Dilute to 1000 ml with metal-free water and mix well. This solution is about 0.1N with respect to nitric acid.
4. *Mixed copper, nickel and cobalt standard solution*: 100 $\mu g/ml$ (*Solution B*). Pipette 100 ml of solution A into a 1000-ml volumetric flask. Add 5.4 ml of concentrated nitric acid, dilute to about 900 ml with metal-free water, mix and allow to cool to room temperature. Dilute to 1000 ml with metal-free water and mix well. This solution is about 0.1N with respect to nitric acid.
5. *Mixed copper, nickel and cobalt calibration solutions*: These are prepared according to the dilutions listed in Table II.
6. *IN HNO_3*: Dilute 125 ml of concentrated HNO_3 to 2,000 ml with metal-free water. Store in a polyethylene bottle.

TABLE II — Mixed Copper, Nickel and Cobalt Calibration Solutions

Concentration ($\mu g/ml$)	Volume of Solution A(ml)	Volume of Solution B(ml)	Volume of Concentrated HNO_3 (ml)	Final Volume (ml)
0.5	—	1	12.5	200
1.0	—	2	12.5	200
2.0	—	4	12.5	200
4.0	—	8	12.5	200
6.0	—	12	12.5	200
8.0	—	16	12.5	200
10.0	—	20	12.5	200
15.0	3	—	12.5	200
20.0	4	—	12.5	200
25.0	5	—	12.5	200
30.0	6	—	12.5	200
35.0	7	—	12.5	200
40.0	8	—	12.5	200