SEMI-MICRO DETERMINATION OF FERROUS SULPHIDE IN SHALES

By S. NEGLIA and L. FAVRETTI,
Agip Mineraria, Servizio Geochimico, Milano, Italy.

[Received 3rd November, 1961]

ABSTRACT
A new method is described for determining in shales the amount of sulphides that dissolve in dilute hydrochloric acid. The samples are treated with hydrochloric acid under vacuum, and the hydrogen sulphide evolved is absorbed in potassium hydroxide and titrated with potassium permanganate. The analytical results are expressed as FeS.

INTRODUCTION
During a study of the distribution of the sulphur content in Triassic black shales of the Sicilian basin, it has been observed that in addition to a considerable amount of pyrite (up to 6 per cent. by weight), there were present also small amounts of HCl-soluble sulphides that were easily detectable from the H$_2$S evolved. An attempt to determine the total amount of these sulphides separately has led to the development of a new analytical procedure based on reaction of the samples with dilute hydrochloric acid under vacuum, absorption of the H$_2$S in potassium hydroxide, and titration with potassium permanganate.

In comparison with the method described by Scott (1956) this new procedure has the advantages of being more rapid and of requiring much smaller samples (only 50-150 mg as compared with 1-5 g). It can, therefore, be used in routine analysis of recent or ancient sediments even when, as often happens, only small samples are available. Moreover, preliminary treatment of the sample with hydrochloric acid enables better determination of pyrite by the nitric acid method previously described (Neglia, 1961). The filtered and washed residue after reaction with hydrochloric acid (the filter paper is not appreciably oxidized by nitric acid*) can be used directly for the pyrite determination. Interference due to sulphides, and to ferrous iron present as carbonate or silicate attacked by HCl, is thus eliminated.

ANALYTICAL PROCEDURE
A weighed portion of 50-150 mg of the pulverized sample is placed in flask $A$ (Fig. 1), 50 ml of 5 per cent. potassium hydroxide solution poured into flask $B$ and the various parts of the apparatus assembled

*One no. 5892 9 cm diameter Schleicher and Schull filter paper treated with a 32.5 per cent. by weight solution of nitric acid reduces only 0.02 ml 0.1 N KMnO$_4$. 

37
The apparatus is then evacuated by a rotary pump. After closing stopcock $S$, the connection to the vacuum pump is removed, 10 ml of 2N hydrochloric acid poured into $C$, and, by opening $S$, into flask $A$.

The magnetic stirrer $M$ assists the evolution of $H_2S$, which is readily absorbed by the potassium hydroxide in $B$. After 10 min the solution in $A$ is heated and boiled for 5 min, then 5 ml of 2 per cent. sodium carbonate solution are rapidly poured into $A$. The

$CO_2$ evolved displaces all the $H_2S$ from $A$ to $B$. During the acid treatment it is advisable to shake the apparatus occasionally to assist absorption of the $H_2S$ by the potassium hydroxide. When the reaction is complete, stopcock $S$ is opened to allow entry of air into the apparatus.

The potassium hydroxide solution in $B$ is rapidly transferred to a 250 ml beaker containing 25 ml of 6N sulphuric acid and 5 ml of 0·1N potassium permanganate, measured with a micro-burette. The
DETERMINATION OF FERROUS SULPHIDE

A glass tube connected to flask B must be below the surface of the solution in the beaker, to avoid air oxidation of the KHS formed, and the solution must be stirred with a glass rod. At the end of the operation the walls of flask B are washed with distilled water.

For the titration, the solution in the beaker, which amounts approximately to 100 ml, is heated to about 75°C, 5 ml of 0.1N sodium oxalate added and the excess of oxalate titrated with 0.1N potassium permanganate to a faint pink colour.

DISCUSSION

The reactions taking place during the decomposition of sulphides and H₂S absorption are as follows:

\[
{\text{FeS + } 2H^+ \rightarrow Fe^{2+} + H_2S}
\]

\[
{\text{H}_2S + OH^- \rightarrow H_2O + HS^-}
\]

\[
5HS^- + 8MnO_4^- + 19H^+ \rightarrow 5SO_4^{2-} + 8Mn^{2+} + 12H_2O
\]

From these equations the stoichiometric equivalence is:

\[
1 \text{ ml } 0.1N \text{ KMnO}_4 = 1.099 \text{ mg FeS}
\]

In the samples investigated in this laboratory the analytical results are normally expressed as FeS, because the exact nature of the sulphides (pyrrhotine, hydrotroilite, etc.) is rarely known.

The efficiency of this method has been studied in detail. Comparison determinations with the evolution method (Scott, 1956), performed either on shales or on artificial mixtures in the range of 0.30-3.00 per cent. FeS, have shown a fairly good agreement, especially in the samples with a content of FeS below 1 per cent. (Table 1). For samples with a sulphide content higher than 1 per cent. the H₂S absorption becomes incomplete and the FeS values obtained with the new method are systematically lower than those obtained with the evolution method (Table 1). It is necessary, therefore, to limit

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of determinations</th>
<th>FeS by evolution method (%)</th>
<th>FeS by new method (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>0.35 ± 0.02</td>
<td>0.36 ± 0.02</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>0.88 ± 0.02</td>
<td>0.90 ± 0.02</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>1.20 ± 0.02</td>
<td>1.13 ± 0.02</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>2.99 ± 0.02</td>
<td>2.89 ± 0.03</td>
</tr>
</tbody>
</table>

*Weight of sample, 2 g.  †Weight of sample, 150 mg.

the amount of sample to be analysed, so that the quantity of H₂S evolved will be not higher than that equivalent to 1.5 mg FeS. As the amount of FeS in shale samples is normally below 1 per cent., any modification of the absorption apparatus is unnecessary.
A statistical study of reproducibility on a black shale sample with 1.02 per cent. FeS shows that the average deviation from the mean is not greater than 3.5 per cent., even using very small amounts of sample (Table 2).

**Table 2—Results of reproducibility tests on a black shale with 1.02 per cent. FeS.**

<table>
<thead>
<tr>
<th>Weight of sample (mg)</th>
<th>Number of determinations</th>
<th>Average deviation from the mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>20</td>
<td>3.5</td>
</tr>
<tr>
<td>100</td>
<td>32</td>
<td>2.6</td>
</tr>
<tr>
<td>150</td>
<td>33</td>
<td>1.9</td>
</tr>
</tbody>
</table>

In order to obtain good analytical results the following precautions should be taken:

(a) Before each new series of analytical determinations, a blank should be run to ensure that the reagents used, especially the potassium hydroxide, are free from reducing substances.

(b) As the sulphides are easily oxidizable, especially in the presence of moisture, it is necessary to grind, weigh and analyse the samples as rapidly as possible.

**Acknowledgements.**—The authors desire to thank the Director of Agip Mineraria for permission to publish this paper. Their thanks are also due to Dr G. Long, Director of the Laboratory, and to Mr G. C. Micheletti, who carried out the analytical determinations.

**References**
