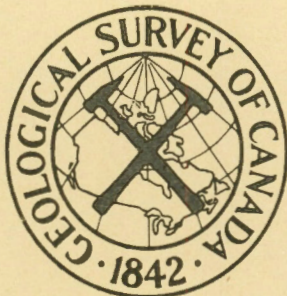


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A RAPID DETERMINATION OF TOTAL ORGANIC AND
INORGANIC CARBON IN SHALES AND CARBONATES

A RAPID DETERMINATION OF TOTAL SULPHUR
IN ROCKS AND MINERALS

(Report and 2 figures)

A. E. Foscolos and R. R. Barefoot

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DEPARTMENT OF ENERGY, MINES AND RESOURCES

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Price: \$1.50

Catalogue No. M44-70-11

Price subject to change without notice

Information Canada

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1970

1972

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ABSTRACT

Procedure and apparatus for determining inorganic and organic carbon in shales and carbonates are described. Results obtained by the proposed method are comparable to those obtained by (i) the United States Geological Survey, (ii) other analysts, and (iii) X-ray diffraction; they are accurate and reproducible. The method is very rapid.

A RAPID DETERMINATION OF TOTAL ORGANIC AND INORGANIC CARBON IN SHALES AND CARBONATES

INTRODUCTION

There are many conventional methods for measuring carbon content (Allison, L. E., 1965; Anderson, J. U., and Harris, W., 1967; Hillebrand, W. F., et al., 1953). One of the more rapid conventional methods is to measure first the total carbon, and then the inorganic carbon, the organic carbon being the difference (Maxwell, J. A., 1968). In the faster method proposed here, the total carbon and the organic carbon are both measured directly, the inorganic carbon being the difference. This is accomplished by weighing two equal portions of the sample and then treating one of the portions with concentrated hydrochloric acid while heating to boiling (this removes the inorganics). A Leco induction furnace with a carbon analyzer is then used to determine the total carbon in both the treated and untreated portions of the sample. Thus, only one instrument is used and extremely fast analyses can be made.

The sample is placed in a combustion crucible and ignited in a current of oxygen in a combustion tube by means of an induction coil. About one gram of iron added to the sample supplies a conductible mass which can be ignited by means of the induction coil. About one gram of tin added to the sample serves as a fluxing material. At high temperatures carbon dioxide, carbon monoxide and sulphur dioxide are formed. These gases are carried, by the flow of oxygen, through a sulphur trap and a catalytic furnace which converts carbon monoxide to carbon dioxide. Thus, the only gases emerging from the system are carbon dioxide and oxygen, and these displace a measurable volume of dilute sulphuric acid which will not absorb them. The gases are then passed through a potassium hydroxide solution which removes the carbon dioxide. The volume of remaining gas, which is oxygen, is then measured, the difference between this volume and that of the original gases being the volume of the carbon dioxide removed. The Leco carbon analyzer measures this volume directly in per cent carbon, which is corrected for temperature and atmospheric pressure by means of a chart. Each carbon analysis takes about 5 minutes.

PROCEDURE

APPARATUS: A Leco induction furnace, complete with catalytic furnace for converting carbon monoxide to carbon dioxide and a purifying train to remove water, carbon dioxide and sulphur compounds from the (oxygen) gas flow, was used (Fig. 1).

A Leco, hand-operated or a semi-automatic gasometric carbon analyzer can be used, although the latter is preferable when running large numbers of samples (Fig. 1).

The porous combustion crucibles used were carbon-free, and each crucible is used for one analysis only.

Original manuscript submitted by authors: 21 May 1970

Final version approved for publication: 3 June 1970

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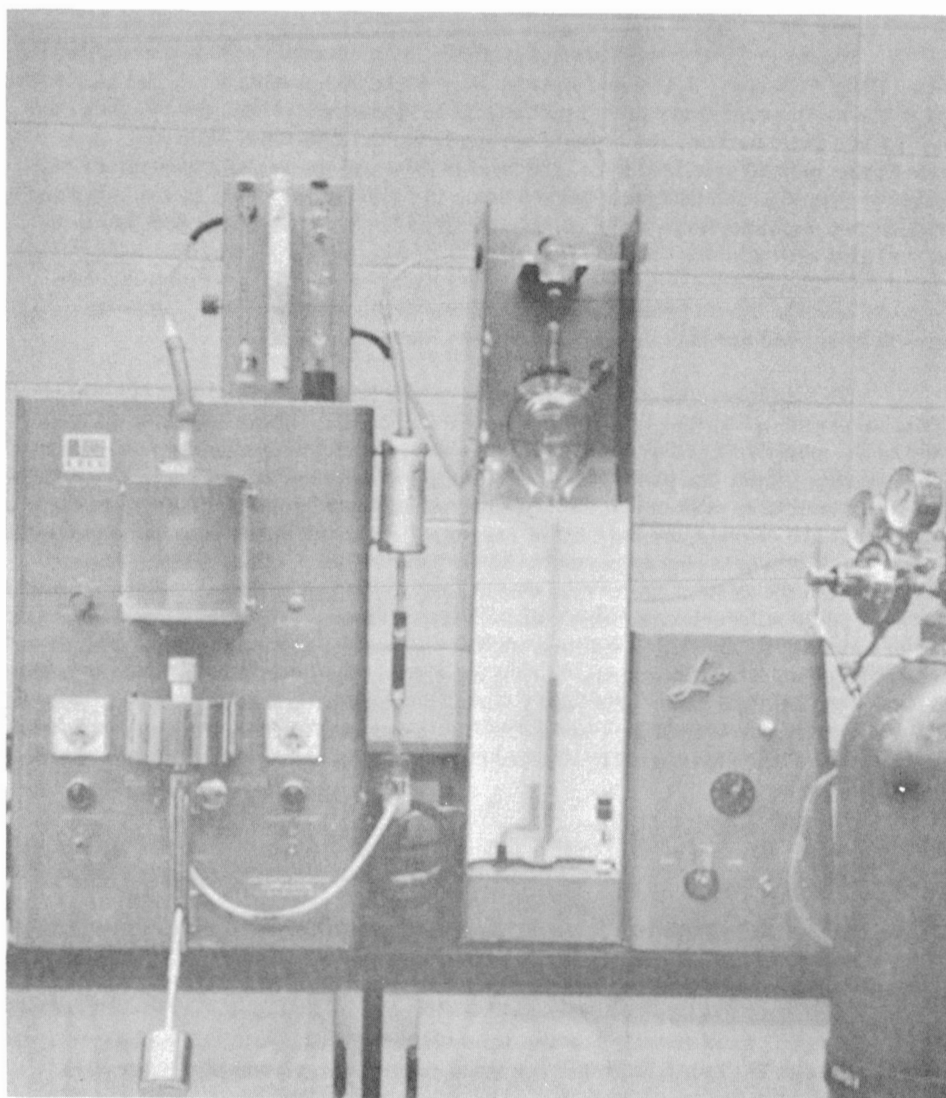


Figure 1. Leco induction furnace No. 521-000 with semi-automatic carbon determinator No. 572-100.

A good mercury barometer should be used because the analysis is based on the measure of the volume of carbon dioxide gas evolved, which is markedly affected by changes in atmospheric pressure.

REAGENTS: The red levelling solution was prepared by boiling for 5 minutes 0.4 grams of methyl orange to which 200 ml of double-distilled water had been added. The solution was cooled in a water bath and then filtered through #50 filter paper, using a vacuum. The filtrate was diluted to 800 ml after which 40 mls of concentrated sulphuric acid was cautiously added. To this solution 2 mls of wetting agent was added (this solution lasts indefinitely).

The potassium hydroxide solution was prepared by dissolving 900 grams of certified potassium hydroxide in 1,800 ml of double-distilled water (this solution is good for about 2,000 analyses).

PROCEDURE: In each of two combustion crucibles place 1,000 mg of sample (0.00 - 1.50%C), or 250 mg (0.00 - 6.00%C), or 125 mg (0.0 - 12.0%C), or 62.5 mg (0.0 - 24.0%C). It is advantageous to have some prior knowledge of the composition of the sample, such as that obtained from X-ray diffraction, or an acid test for carbonates. For example, if the sample was suspected to consist mostly of carbonates, it should contain at least 10% total carbon. Thus the quantity of sample to be weighed should be 62.5 mg.

Fill one of the crucibles, containing sample, about three-quarters full with concentrated hydrochloric acid and immediately place on a hot plate in a fume hood. The plate should be hot enough to keep the bottom third of the outside of the porous combustion crucible dry while the solution boils. Thus everything which is lost during treatment is lost as a gas. When the crucible is completely dry and fumes are no longer visible, remove the crucible and cool.

To each of the two crucibles add 1 gram of iron and 1 gram of tin. Using the Leco induction furnace with carbon analyzer, determine first the total-carbon reading from the untreated sample and, secondly, the organic-carbon reading from the acid and heat-treated sample. The readings obtained must be corrected for expansion or contraction of the measured gas using the provided chart. The gas is being cooled, owing to temperature and pressure changes. The difference between the two readings is the per cent mineral carbon.

RESULTS AND DISCUSSION

The accuracy of the carbon analyzer is borne out by the results of frequent checks on iron ring standards as well as other carbon standards (Tables 1 and 2).

The method proposed is comparable in accuracy with standard methods used by the United States Geological Survey (U.S.G.S.) as shown by the results in Table 3. The method employed by the U.S.G.S. was to determine the total carbon using a Leco carbon analyzer, the inorganic carbon gasometrically, and the organic carbon by difference. The only major discrepancy occurs in the analysis of sample no. D1337791. The total per cent carbon reported by the U.S.G.S. was 2.92 but, upon repeating the analysis several times, the average result obtained by the present method was 4.12.

Results obtained on U.S.G.S. standards are comparable also with those obtained by other analysts (Table 4).

Tests have shown that no organic matter is lost during acid and heat treatment; the amount of carbon is the same before treatment and after treatment, when no inorganic carbon is present as shown by X-ray diffractograms (Table 5). Table 5 also shows the excellent reproducibility obtained.

By estimating the approximate per cent composition of the mineral constituents using the peak heights of primary X-ray diffraction peaks, it is possible to calculate the per cent carbon. For example, 100% calcite contains 12.0% carbon (by formula). Since X-ray diffraction does not include amorphous material or organic matter, and is affected by degree of crystallinity and density, the assigned mineral compositions are only crude estimates. The organic factor can be eliminated by multiplying the per cent organic carbon, found by the Leco carbon analyzer, by 1.72 (Van Bemmelen factor) and then considering this component in the other calculations which bring the total composition to 100%. The comparison of mineral carbon calculated from X-ray diffractograms with those determined by the Leco carbon analyzer using the suggested method, shows the results to be similar (Table 6).

The results obtained by the proposed method are thus accurate and reproducible; the method itself is rapid in comparison with conventional methods. About 25 samples can be analyzed for per cent total, organic and mineral carbon within one working day. Since organic matter can be estimated from organic carbon, a total of 100 analyses can be done easily in one day.

TABLE 1
ACCURACY OF LECO CARBON ANALYZER WITH
INORGANIC AND ORGANIC COMPOUNDS

Sample	% Carbon by Formula	% Carbon by Leco
Calcium Carbonate	12.0	12.0
Lithium Carbonate	16.1	16.0
Sodium Bicarbonate	14.2	14.1
Potassium Hydrogen Phtalate	46.5	45.4
Sodium Oxalate	18.0	17.9

Note: The "% Carbon by formula" was corrected for purity.

TABLE 2

ACCURACY OF LECO CARBON ANALYZER
WITH LECO RING STANDARDS

Standard	% Carbon Certified	% Carbon by Leco
Iron Ring Standard	0.373	0.378
Iron Ring Standard	0.654	0.651
Iron Ring Standard	0.922	0.920

TABLE 3

COMPARISON OF U. S. G. S. RESULTS
WITH I. S. P. G. RESULTS

Sample Serial No.	Carbon %					
	Total		Mineral		Organic	
	U. S. G. S.	I. S. P. G.	U. S. G. S.	I. S. P. G.	U. S. G. S.	I. S. P. G.
D1337788	7.72	7.60	4.52	4.34	3.2	3.2
D1337789	5.59	5.80	0.85	0.68	4.7	5.1
D1337790	3.72	3.75	0.17	0.04	3.6	3.7
D1337791	2.92	4.12	0.16	0.20	2.8	3.9
D1337792	3.46	3.50	0.07	0.06	3.4	3.4
D1337793	7.68	7.62	5.43	5.02	2.2	2.5
D1337794	2.78	2.82	0.86	0.70	1.9	2.1
D1337795	3.03	3.19	1.58	1.40	1.4	1.8
D1337796	6.27	6.23	5.63	5.71	0.6	0.5
D1337797	1.48	1.71	1.34	1.30	0.1	0.4

TABLE 4

DETERMINATION OF CARBON DIOXIDE
IN U. S. G. S. STANDARDS

Sample	Mineral % C By Leco	Calculated* % CO ₂	Reported % CO ₂
GSP-1	0.033	0.12	0.14
AGV-1	0.014	0.05	0.05
PCC-1	0.049	0.18	0.12
DTS-1	0.007	0.02	0.07
BCR-1	0.005	0.02	0.03
G-2	0.006	0.02	0.08

* Calculated % CO₂ obtained by multiplying Mineral
% C x 3.66

TABLE 5
EFFECT OF ACID AND HEAT TREATMENT
ON ORGANIC CARBON

Shale Samples	Carbon %			
	Total	Organic	Mineral	
			By Diff.	By X-ray
7BR-63D	1.34	1.34	0.00	0.0
8BR-3(55)	15.52	15.52	0.00	0.0
8BR-4A	0.20	0.20	0.00	0.0
16BR-1A	4.14	4.14	0.00	0.0
16BR-1L	5.85	5.85	0.00	0.0
17BR-2A	3.50	3.50	0.00	0.0
Si-64-829	0.98	0.98	0.00	0.0
Si-64-880	1.07	1.07	0.00	0.0
Si-64-1062	0.84	0.84	0.00	0.0

Note: 1) BR - samples are from shale outcrops in the
Yukon; collected by Dr. W. Bamber of I.S.P.G.

2) Si - samples are from outcrops in British
Columbia; collected by Dr. D. F. Stott of I.S.P.G.

TABLE 6
COMPARISON OF X-RAY DIFFRACTION ESTIMATES
WITH LECO MINERAL CARBON RESULTS

Sample	% Mineral Carbon	
	By Leco	By X-ray
4 BR-9A	0.12	0.2
4 BR-11A	1.42	1.3
4 BR-13A	0.00	0.0
8 BR-4B	1.75	2.3
43 BR-4E	5.82	5.7
43 BR-4F	5.81	6.0
YTM-59#1	3.57	4.5
YTM-49#4	0.68	0.7
YTM-59#8	7.46	7.8
YTM-59#9	1.29	1.2
YID-77-750	0.50	0.4
YID-77-1060	4.57	5.1
YID-77-1650	0.00	0.0
YID-77-2210	0.46	0.4

Note: 1) BR - samples are from shale outcrops in the Yukon; collected by Dr. W. Bamber of I.S.P.G.

2) Y - samples are core samples collected by H. Martin of I.S.P.G.

3) X-ray results are crude estimates

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A RAPID DETERMINATION OF TOTAL SULPHUR IN ROCKS AND MINERALS

ABSTRACT

Procedure and apparatus for determining sulphur in rocks and minerals are described. Results obtained for United States Geological Survey standards, standard chemicals and other sulphur standards are accurate and reproducible. The method is extremely rapid.

INTRODUCTION

A common method of determining total sulphur is to decompose the sample in an oxidizing environment thereby converting sulphur to sulphate which, when dissolved, will, upon the addition of barium chloride, precipitate out as barium sulphate (Assoc. Offic. Agril. Chemists, 1955; Goldich, S. S., et al., 1959; Shapiro, L., et al., 1962; Wilson, A. D., et al., 1963). This is obviously applicable to samples which have an appreciable amount of sulphur.

Determining small amounts of sulphur in samples can be accomplished by igniting the sample in a current of oxygen, producing sulphur dioxide which is absorbed in an excess of potassium iodate - iodide solution; the excess is then back-titrated with thiosulphate solution (Sen Gupta, J. G., 1963).

These two methods have at least one drawback, they take considerable time per determination.

A much more rapid and accurate method is the use of a Leco induction furnace with an automatic sulphur titrator. The sample is placed in a combustion crucible (sulphur-free) and ignited in a current of oxygen in a combustion tube by means of an induction coil. About one gram of iron (sulphur-free) added to the sample supplies a conductible mass which can be ignited by the induction coil. About one gram of tin (sulphur-free), added to the sample, serves as a fluxing material. Within one minute the sample temperature is up to 2000° C and the sulphur is converted to sulphur dioxide which is immediately and automatically titrated with a potassium iodate-iodide solution giving the readout in per cent sulphur. The whole process takes about four minutes, which is considerably less time than other rapid techniques (Bloomfield, C., 1962; Sen Gupta, J. G., 1963). Calibrated burets with the ranges 0.000 to 0.200% S and 0.00 to 4.00% S are available. Greater sulphur concentrations can be determined by decreasing the weight of the sample or by increasing the strength of the titrant, or both.

PROCEDURE

APPARATUS: A Leco induction furnace, with a purifying train to remove water and sulphur compounds from the oxygen flow, was used (Fig. 2).

A Leco automatic sulphur titrator was used, in which titration proceeds continuously by means of an electronic circuit and the end point is arrived at automatically. A semi-automatic titrator can be used also (Fig. 2).

The porous combustion crucibles used were sulphur-free. Each crucible is used for only one analysis; they are, however, inexpensive.

REAGENTS: A potassium iodate solution (1 ml $\text{KIO}_3 = 0.2 \text{ mg S}$) was prepared by dissolving 0.4450 g KIO_3 in double-distilled water in a one-liter volumetric flask and diluting to volume. The buret range for this solution is 0.000 to 0.200% sulphur. A larger buret with a range of 0.00 to 4.00% sulphur was used also. Multiples of these ranges can be obtained by preparing potassium iodate solutions with corresponding multiples of 0.4450 g KIO_3 .

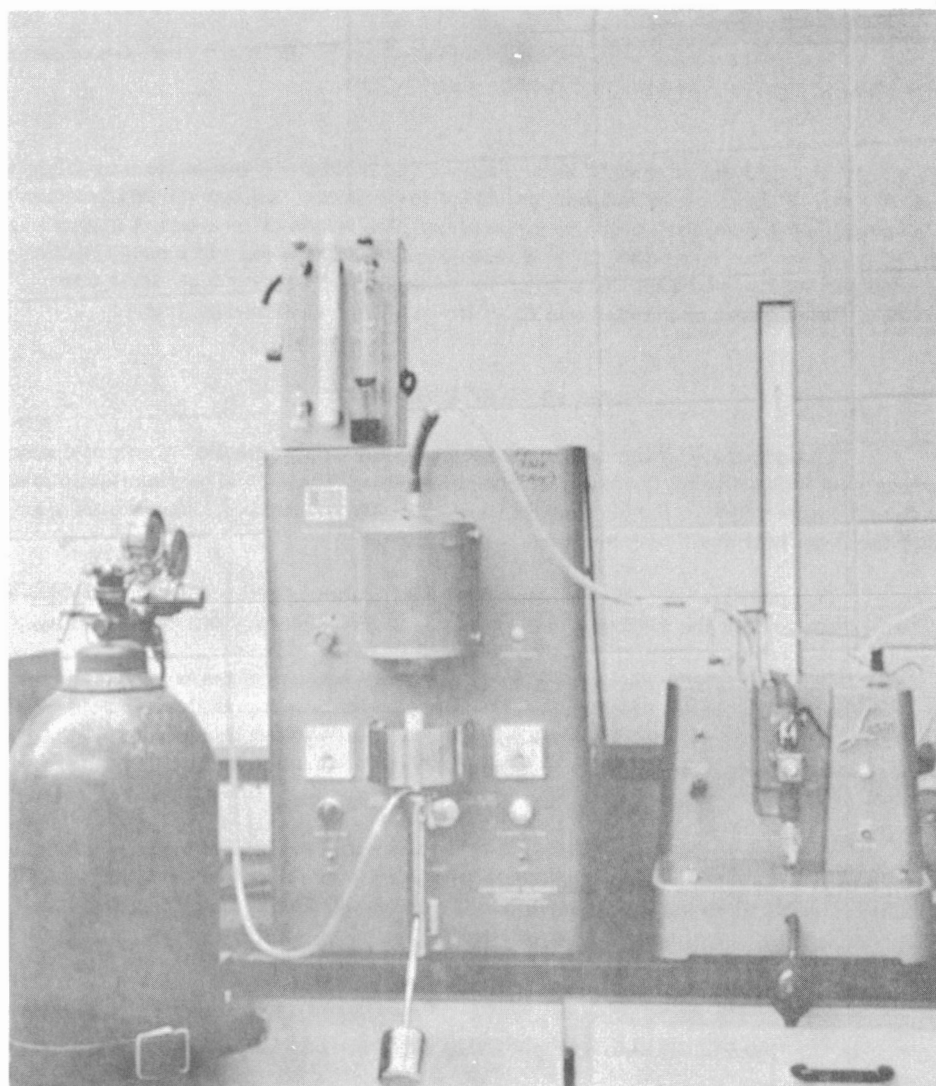


Figure 2. Leco induction furnace No. 521-000 with fully automatic sulphur titrator No. 532-000.

The starch solution was prepared by adding 2 grams of Arrowroot starch to 50 ml of double-distilled water and stirring. This mixture was then added to 150 ml of boiling double-distilled water while stirring. After 2 minutes of boiling it was cooled to room temperature and 6 grams of potassium iodide added.

The hydrochloric acid solution was prepared by diluting 15 ml of concentrated hydrochloric acid to 1,000 ml with double-distilled water.

PROCEDURE: 125 mg of sample were weighed and placed in a combustion crucible (0.00 to 4.00% S). If the per cent sulphur was found to be higher, an appropriate fraction of this weight, or a stronger titrant could be used. One scoop of iron (about 1 gram) and one gram of tin flux were added. The sample was placed in the Leco induction furnace, the acid and starch solutions were added to the automatic titrator and, after a few minutes, the per cent of sulphur was read directly from the titrating buret.

RESULTS AND DISCUSSION

The accuracy of the sulphur determinations was borne out by frequent checks on iron ring standards for low sulphur concentrations, Table 1, and by chemical standards such as ferrous sulphate for high sulphur concentrations, Table 2. These tables also show the good reproducibility obtained.

Comparison with other accepted methods, shown by the results in Tables 3 and 4, demonstrates that the proposed method is of similar accuracy and reproducibility.

Since smaller amounts of sample and a stronger titrant are necessary for determining high sulphur concentrations, some precision is lost and small errors are introduced, Table 5. However, since good reproducibility was obtained, the purity of some of the chemicals used, such as ammonium sulphate and sodium bisulphite, is suspect.

Not only is the described method accurate and reproducible for determining sulphur over a wide range, but it is extremely rapid. In one 8-hour working day it is possible to do up to 80 sulphur determinations on samples of rocks and minerals.

TABLE 1

DETERMINATION OF LECO SULPHUR STANDARDS

Standard	% Sulphur Certified	% Sulphur By Leco	
Iron Ring Standard	0.031	0.031	0.031
Iron Ring Standard	0.021	0.021	0.021
Iron Ring Standard	0.012	0.013	0.013
Iron Ring Standard	0.014	0.015	0.015
Iron Ring Standard	0.020	0.020	0.020

TABLE 2

DETERMINATION OF SULPHUR IN FERROUS
AMMONIUM SULPHATE ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)

% Sulphur By Leco	% Error
11.5	0.0
11.6	+0.1
11.4	-0.1
11.5	0.0
11.4	-0.1
11.6	+0.1
11.5	0.0
11.5	0.0
11.5	0.0
11.5	0.0

TABLE 3

DETERMINATION OF SULPHUR IN U. S. G. S. * STANDARDS

Standard	% Sulphur Reported**	% Sulphur By Leco	
GSP-1	0.05	0.04	0.04
AGV-1	0.01	0.01	0.01
PCC-1	0.01	0.01	0.01
DTS-1	0.01	0.01	0.01
BCR-1	0.05	0.05	0.05
G-2	0.02	0.01	0.01

* U. S. G. S. - United States Geological Survey

** Results obtained by Geological Survey of Canada

TABLE 4

COMPARISON OF I. S. P. G. * RESULTS WITH GSC** RESULTS

Sample	% Sulphur	
	I. S. P. G.	GSC
138-65	1.17	1.17
139-65	2.72	2.72
140-65	6.08	6.27
CAAS Std.	12.0	12.1

* I. S. P. G. - Institute of Sedimentary
and Petroleum Geology

** GSC - Geological Survey of Canada

TABLE 5

DETERMINATION OF HIGH SULPHUR CONCENTRATIONS

Sample	% Sulphur		
	By Leco	By Formula	
Silver Sulphate	10.2	10.2	10.3
Ammonium Sulphate	22.5	22.7	24.3
Ferrous Sulphate	11.5	11.5	11.5
Potassium Pyrosulphate	23.8	23.8	24.3
Potassium Sulphate	18.3	18.2	18.4
Sodium Bisulphate	23.1	23.2	23.2
Sodium Bisulphite	30.4	30.3	29.0
Sodium Thiosulphate	39.6	39.7	40.3
Zinc Sulphate	11.0	11.0	11.1

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