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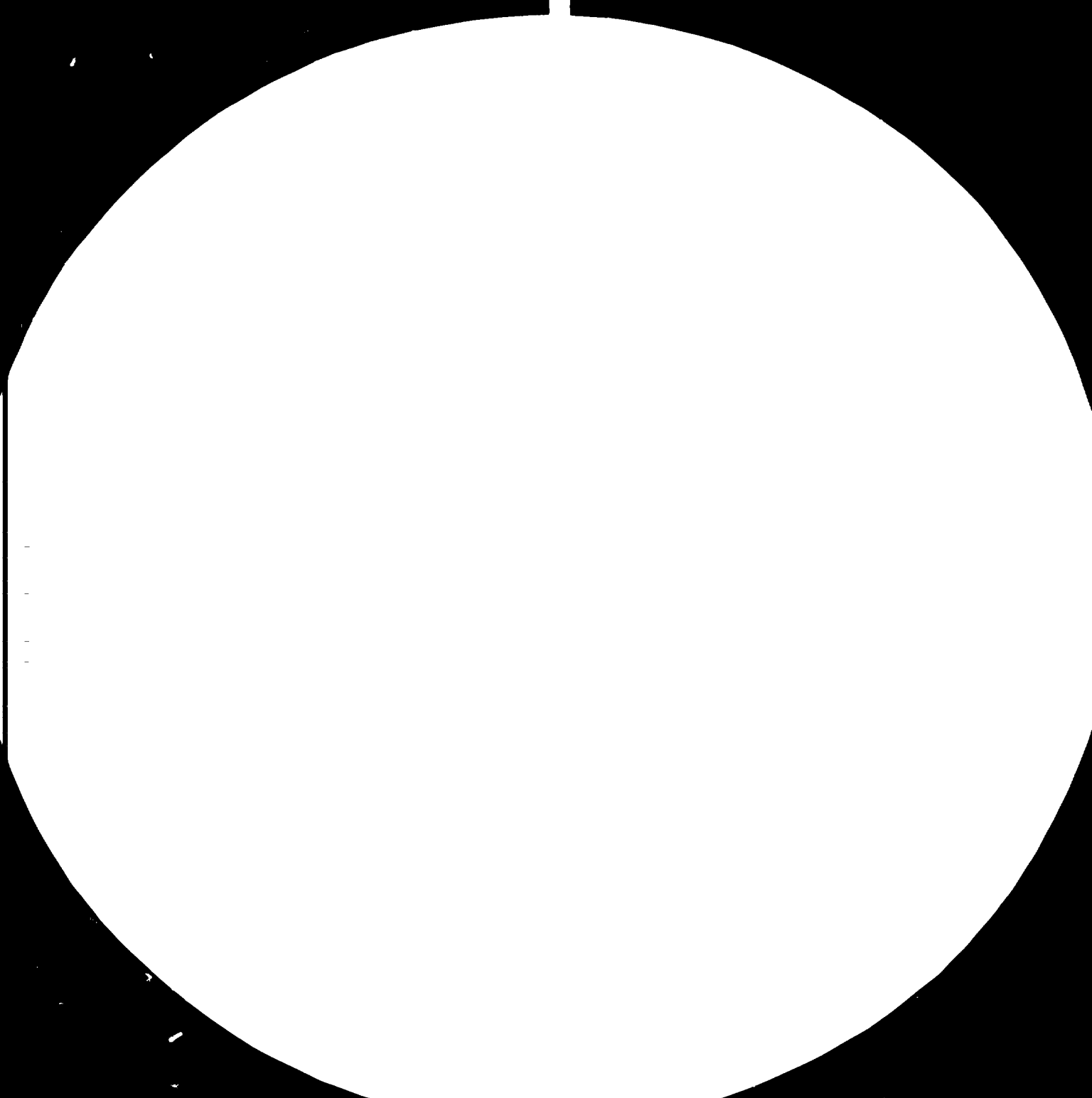
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2.8



3.2



3.6



4.0



Resolution test patterns are used to measure the resolution of a system. The resolution is the number of lines per inch (LPI) that can be resolved. The resolution is measured by the number of lines that can be resolved in a given area. The resolution is measured by the number of lines that can be resolved in a given area.

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DEVELOPMENT OF BRICKMAKING INDUSTRY
AND
INVENTORY OF INDUSTRIAL CERAMIC RAW MATERIALS

DP/MLW/78/003

REPUBLIC OF MALAWI

Technical Report: Assessment of Analytical Chemical Methods
Applied in Non-metallic Mineral Testing *

Prepared for the Government of
the Republic of Malawi
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of Anna Marabini,
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United Nations Industrial Development Organization
Vienna

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INTRODUCTION

In 1979, as part of a programme to develop the brickmaking and ceramic industries, the Malawi Government requested the services of a consultant analytical chemist through the United Nations Industrial Development Organization (UNIDO). Within an on-going project DP/MLW/78/003, provision was made for up to four visits of two months each for the consultant. The consultant was expected to:

- Examine the range of present and future analysis requirements
- Check on working methods, laboratory apparatus and equipment
- Assess the skills of the technical personnel
- Review the existing analytical methods
- Set out recommendations for improving or reviewing existing settlement and analytical methods.

I. ANALYTICAL NEEDS

A) Present Analyses

SAMPLES	ANALYSED CONSTITUENTS	
	Commonly required	Occasionally required
ROCKS AND SILICATE MATERIALS	SiO_2 Al_2O_3 Fe_2O_3 CaO MgO K_2O Na_2O TiO_2	Loss of ignition MnO $\text{H}_2\text{O}+$ $\text{H}_2\text{O}-$ P_2O_5 Cr_2O_3 CaO

<p>LIMESTONES</p>	<p>CaO MgO</p> <p>INSOLUBLE</p>	<p>Al₂O₃) Na₂O) for cement manufacturing K₂O)</p> <p>SiO₂) for sugar and pharmaceutical) manufacturing</p> <p>Fe₂O₃) as flux for Al₂O₃) glass manufacturing</p>
<p>GLASS SANDS</p>	<p>Al₂O₃ Fe₂O₃ CaO MgO K₂O Na₂O</p>	<p>Loss of ignition</p> <p>Cr₂O₃ CoO MnO</p>
<p>SALTY SOIL</p>	<p>SALT CONTENT</p> <p>Na K Ca Mg Fe F⁻ Cl⁻ NO₃⁻ CO₃ SO₄</p> <p>Conductivity measure- ments pH</p>	

B) Future Anticipate Analyses

SAMPLES	ANALYSES REQUIRED
APATITES	P_2O_5
COAL	Full Chemical analysis of ash Sulphur
URANIUM MINERALS	U_3O_8

II. ASSESSMENT OF THE SKILLS OF THE LABORATORY STAFF

This is the staff in the analytical laboratory:

Mr. P. MUMBA	B.Sc. (Hons) Bachelor of Science (newly employed, approx. 2 weeks)
<u>Mr. R. BANDA</u>	Senior Laboratory Technician
<u>Mr. C. BANDA</u>	Senior Laboratory Assistant
Mr. M.C. MPEZENI	Technical Assistant (new in laboratory)
<u>Mr. M.B. CHITETE</u>	Laboratory Assistant
<u>Mr. M.M. CHEYETSE</u>	Laboratory Assistant
Mr. A. Maliro	Laboratory Assistant (new, approx. 2 weeks)
Mr. T. NOWA	(newly employed, temporary)
Mr. T.P. PEMBA	Cleaner

Sample preparation:

Mr. A. KASAWALA	Laboratory Attendant
Mr. M. LABANA	Laboratory Attendant
Mr. D.K. JIMU	Laboratory Attendant (new, approx. 2 months)

On the whole four people attend at present to analytical work. Mr. R. Banda is the Head of the laboratory. The Technical assistants perform pure executive duties and follow orders of the Messrs R. and C. Banda. Their activity is generally limited to some particular analytical techniques, that is they can run a complete analysis on routine basis but need occasional supervision. Messrs. R. and C. Banda are the real people who support the laboratory. Both of them work seriously and with great care and accuracy. Mr. C. Banda is able to run a complete analysis following the written procedure, except for the final calculations. Mr. R. Banda is gifted with keen intelligence, cleverness, observing attitude and practical temperament.. He can run new methods up to and including final calculations. However, his working method could be improved

to increase efficiency (speed) at which analyses are carried out. This could be achieved by limited training in another laboratory. He has a real aptitude for instrumental analysis and general familiarity with scientific instruments. Therefore, Mr. R. Banda can be considered able to operate on new, even more sophisticated instruments after an adequate period of training.

III. CHECK ON WORK - METHODS, LABORATORY APPARATUS
AND EQUIPMENT

Remarks and recommendations are made following the sequence of the analytical procedures starting from the arrival of the sample in the chemical laboratory up to the final analytical results.

A) ANALYSIS REQUIREMENTS

Findings

The sample arrives in the laboratory accompanied by a small leaflet on which the elements required for the analysis are written.

Recommendations

It is recommended that printed pads of Analysis Requisition forms be used similar to the specimen submitted by the expert. One copy will be loosened and enclosed to a similar form containing the analytical results. The nature of the sample and the presumed content (if possible) should be indicated.

B) SAMPLE PREPARATION

Findings

The current procedure of sample preparation is not correct. The amount of the sample given to the laboratory is always nearly the same (from 0.5 to 2 kgs) whatever the grain size may be. The crushing, grinding and sampling are hand-made and these manual operations are unable to produce effective results in terms of quality and quantity of output.

Recommendations

To ensure that the materials which arrive in the laboratory are representative of the exposure from which they have been taken, great care must be taken in the size of the sample.

A representative specimen will vary with the mineral grain size. Table A or Diagram No. 1 can indicate to geologists the approximate size of samples that should be collected, so that the results of chemical analyses can represent the real chemical composition of the material.

TABLE A

Weight of Rock Material that Should Be Collected

Maximum Grain Size (mm)	Weight Suggested (kg)
1	2 $\frac{1}{2}$
5	5
10	10
20	20

By Jeffery - Chemical Methods of Rock Analysis

A small sample (0.2 to 1 g) of fine powder is usually analysed which must be representative of the original specimen. The preparation of this sample must be performed with accuracy and precision.

- Automatic machinery and labor and time saving devices should be used for this operation.

The subsequent stages are recommended:

- a) The sample is fed to a jaw-crusher so that the whole of the sample is reduced in this way to pass a No. 5 mesh sieve (3-4 mm).
- b) This material is riffled to give about 0.5 kg which is sieved on a No. 10 (1-2 mm) mesh sieve; the oversized is fed again to the jaw-crusher on its finest setting. The product is riffled again to give about 100 g of material.
- c) All the sample is subsequently ground in a grinder which may be of the roll disc or coffee mill type, the grinding is stopped when the whole of the sample passed through a 200-mesh sieve.
- d) A rotary-type sample-splitter is then used to reduce the material to the sample needed for the analysis (about 10-20 g).

The equipment recommended for routine analysis is:

1. A jaw-crusher
2. A laboratory riffle (better a series of riffles of varying sizes)
3. A series of sieves
4. A rotary-type sample-splitter

A wide documentation on this equipment, possible models and their main features are reported in Annex No.2.

c) DRYING AND WEIGHT OF THE SAMPLE

Findings and recommendations

Two ovens are in the laboratory, produces by Baird Tarlock Ltd.; one for the glassware drying and one for sample drying. This is sufficient for laboratory needs.

The balance is a single pan analytical balance Mod.R20 produced by L OERTLING Ltd. It was purchased in 1969 and its features do not assure fast and reliable weighing results. A modern electronic analytical balance is recommended.

D) DECOMPOSITION OF THE SAMPLE

Findings and recommendations

- For acid attacks, two hot plates and one water, both are available. At the moment, they are working satisfactorily.

- Two carbolite muffle furnaces are available for fusion procedures, one to 1 400° C, and one to 1 200° C. This supply is adequate at the moment.

- A magnetic stirrer thermostat hotplate produced by Gallenkamp Ltd. is working well and adequate for the present needs.

- It is essential that the fume cupboards and extraction system be completely overhauled or replaced, with replacement being the recommended solution.

- Some indications on possible models of suction hoods, motors and fans are given in Annex No. 3.

- A supply of seven platinum dishes and thirteen crucibles are available at the moment. This is not sufficient: At least, twenty platinum dishes should be in the laboratory; the crucibles are sufficient at the moment.

E) ANALYTICAL PROCEDURE

1. PURIFIED WATER

Findings

There are a "portable-deionizer" and a "distillation unit" to produce pure water. The deionizer is an "Elgastat B 102 Deionizer" produced by Elga products Ltd. The distillation unit is a "BTL Base Mark IV fills" supplied by Baird Tatlock Ltd.

Recommendations

Both of them are working properly, but it is suggested to supply the laboratory with a new Deionizer with better technical features and higher capacity, similar to that shown in Annex 4.

This is on account of the large quantity of pure water necessary to dilute the samples when most of the analyses will be performed by atomic-absorption techniques.

2. GLASS-WARE

Findings and recommendations

There is an adequate supply of general glassware (flasks, cylinders, beakers, burettes, etc.).

- Bulk pipettes with two graduation marks are necessary.
- A supply of automatic pipettes of the type illustrated in Annex No. 5 is necessary. Two specimens have been delivered to the laboratory.
- Rapid filtration funnels and Buchners are recommended.
- A new vacuum pump for vacuum filtration is recommended.

3. INSTRUMENTS

Findings and recommendations

The instruments available in the laboratory are:

1. A "Cecil Instruments Colorimeter Mod. CE 404" equipped with a "440 sampler 11" produced by Hook and Tucker Instruments Ltd.
2. A SP 90 Atomic Absorption Spectrophotometer produced by Unicam Instruments Ltd.
3. A "Flame Photometer" produced by Evans Electro Selenium Ltd supplied with the sodium and potassium filters.
4. A "Direct Reading pH Meter Model 23A" produced by Electronic Instruments Ltd . supplied with specification electrodes for fluoride, calcium and magnesium determination in water analysis.

5. A "Conductivity Bridge Type E 75663" produced by Mullar Equipment Ltd.
6. A "Centrifuge Mod. CF-405 produced by A. Gallenkamp Co. Ltd.
7. A "E 742 Spectrograph" produced by Hilger Watt Ltd. for qualitative analysis.

The Colorimeter was purchased in 1980.

The pH-meter in 1973. All others were supplied around 1965 and 1967. The colorimeter C.E. is a filter photometer: Six standard filters are fitted to the instrument to isolate desired spectral regions; but they do not continuously supply variable and nearly monochromatic bands of light.

At the moment the colorimeter can be used for current analyses, provided that a voltage stabilizer is used. An UV and V double-beam spectrophotometer is suggested of the types shown in enclosure No. 6. The existing AA spectrophotometer must be considered not working correctly and obsolete.

It is called single beam because all measurements are based on the varying intensity of a single beam of light. In such a system all the fluctuations into the mains voltage are translated into fluctuations in source intensity and consequently in fluctuations in instrument readout. Actually it was observed that the readings were made under conditions of maximum noise and instability. This is the principal factor limiting sensitivity and reproducibility of the atomic absorption method. The constant voltage transformer inside the instrument does not supply sufficient stabilization. An efficient voltage stabilizer is absolutely necessary.

The instrument has been used up to now without air pressure control, because the flowmeter was broken. A new flowmeter was installed and now it is possible to measure the flow of both, fuel and air. Nevertheless, the gas and air flow rates are not yet constant, fluctuations in flame temperature consequently giving less precise measurements. Continuous corrections are necessary during the readings. Hollow cathode lamps near the end of their life or sometimes faulty, are often used, resulting in a reduction of atomic absorption sensitivity and poor calibration linearity. The purchase of a new AA double beam spectrophotometer is highly recommended.

In this system the light from the lamp is divided into a sample beam, which is focused through the sample cell, and a reference beam, which is directed around the sample cell to serve as a monitor of lamp intensity. In a double beam system the readout does not simply represent the intensity of a single beam of light, but a ratio of the sample and reference beams, both of which originate from the same source. As a result, fluctuations in source intensity which affect the intensity of both sample and reference beams equally are not translated into fluctuations in instrument readouts. The baseline is therefore much more stable than in a single beam instrument. This freedom from the effect of source intensity drift means that lamps need not be warmed up prior to use resulting in an extension of useful lamp life (the improved baseline stability also makes it easier to use higher scale expansion for the determination of very low concentrations).

Perkin-Elmer AA spectrophotometers of the type illustrated in enclosure No. 7 are highly recommended. The Mood 5000 offers the best performance; the estimated cost is US \$ 40,000 to 45,000; the Mood 4000 has all the features which provide Mood 5000 performance, the only difference being the degree of automation. The cost is around US \$ 25,000. The instruments will cover most of the present and future analytical needs of the laboratory and will make the routine analyses more quick, precise and accurate.

Two burner heads for air-acetylene flame and nitrous oxide-acetylene flame are supplied with either of the instruments. Therefore, even silica and alumina will be quickly and simply determined.

Training is needed for maintenance and operation for some of the personnel. This training may be run in the laboratories of the manufacturing company. The length may be around one month, but it can be better defined by the company itself. Mr. Roger Banda and Mr. Peter Mumba would benefit most from this training. Particularly, Mr. Banda has already a good knowledge of atomic absorption techniques and he will be able to operate new instruments within a short time.

A fume extraction assembly is absolutely necessary on the AA spectrophotometer.

The flame photometer used to determine Na and K in every kind of sample is obsolete and inadequate, especially for low content samples. It has been proved analysing standard samples. Since a flame photometer must be considered one of the best ways of determining sodium and potassium, a new instrument is suggested similar to these shown in Annex No. 8.

Nevertheless, if a new atomic absorption spectrophotometer is purchased, it can also be used for the determination of alkali metals. In this case the cathode lamps usually employed, should be replaced by discharge lamps which give stable, line emissive sources.

With regard to the pH meter and the conductivity bridge, both of them should be replaced by new ones with better and more modern features, this particularly on account of the water analysis.

The centrifuge works properly, but it is not commonly used for analytical work.

The spectrograph has not been tested, but probably even this instrument is inadequate and obsolete.

4. REAGENTS

Findings and recommendations

A wide range of (pure) analytical grade reagents is available in the laboratory. With certain exceptions, the supply is adequate. A supply of standard solution for atomic absorption spectroscopy is absolutely necessary.

F) ANALYTICAL RESULTS

The analytical results must be reported on special forms similar to the attached one (Annex No. 1) in two copies. One copy of the report form is attached to a copy of the requisition form and they are passed on to the Chief Geologist for distribution. The carbon copies of both forms remain in the laboratory as permanent record.

IV. CHECK ON ANALYTICAL METHODS FOR COMMONLY ANALYSED CONSTITUENTS

A) DETERMINATION OF CaO AND MgO IN SILICATE MATERIALS

FINDINGS

Brief outline of the existing method

1 g of sample is dissolved in 10 ml of HNO_3 , 10 ml of HClO_4 and 25 ml of HF. The solution is fumed to dryness and fuming is repeated with 5 ml of HClO_4 . A final solution is made up with 1 ml of HClO_4 and distilled water. The excess of quartz is filtered off and the solution is made up to 100 ml. 0.5 g of sample is occasionally weighed using half the amount of acid for a final solution of 50 ml.

Ca and Mg are determined by AA spectroscopy using different operating conditions every time. The fuel pressure is always about 0.4, and the air pressure is not measured. An all expanded scale is always used.

The decomposition method is generally satisfactory to determine Ca, Mg, Na and K in silicate materials. Nevertheless, to assure a complete decomposition and a complete evaporation of SiO_2 , it is suggested to repeat fuming with HF and HClO_4 as described in the following recommended method. It is also suggested to add a higher amount of HClO_4 to the solution, especially when a high content of iron must be determined also. The AA determination of Ca and Mg is the most preferable method for silicate materials, in comparison with any other method, under suitable conditions with proper equipment. It is simple and rapid and the possibility of errors from the operator are largely reduced. The interferences from Aluminium, phosphates and sulphates can be easily removed by adding lanthanum chloride at a concentration of 0.1 - 1 % to samples and standards. There are many sources of error in the current techniques used in the laboratory to determine Ca and Mg by AA spectroscopy:

- Lack of proper standard solution for AA spectroscopy
- Lamps with reduced intensity (with fault or near the end of their life), as observed for Ca.
- Fluctuation and instability of readings. Low sensitivity. Night detection limit, i.e. faulty instruments.
- Lack of air pressure control, (air flowmeter not working).
- Fluctuations in acetylene and air flow rates.

The inaccuracy of the method has been shown in comparison of results obtained on a series of glass sands with the analytical results obtained by M.C. Lachlan and Lasar Laboratories. Since no other chemical methods (either colorimetric or volumetric) can give better results, the atomic absorption spectrophotometry and flame photometry are at present the only methods suitable for Ca and Mg determination. Since the existing flame photometer does not have Ca and Mg filters, the work concentrated on finding the optimum operating conditions with the atomic absorption spectrophotometer to achieve the best results.

RECOMMENDATIONS

The following procedure has been developed:

Reagents

- Lanthanum Chloride Solution: Dissolve 58.6 g of analytical grade lanthanum oxide by heating with 1 litre of 1-2 N hydrochloric acid. Store in a polyethylene bottle.
- Stock Standard Solution:
Calcium, 500 $\mu\text{g}/\text{ml}$.: To 1.249 g of primary standard calcium carbonate, CaCO_3 , add 50 ml of deionized water. Add dropwise a minimum volume of HCl (approx. 10 ml) to affect complete solution of the CaCO_3 . Dilute 1 litre with deionized water.

Magnesium, 1000 μ g/ml.: Dissolve 1,000 g of clean fresh magnesium ribbon in a minimum volume of (1 + 1) HCl. Dilute to 1 litre with water.

Procedure: Accurately weigh 0.5 g of the finely powdered sample (- 200 mesh) into a platinum dish, moisten with water and add 12 ml HF, 5 ml HNO₃, 5 ml HClO₄. Transfer the dish to a hot plate and evaporate, first to fumes of perchloric acid and then to dryness. Allow to cool. Moisten with a few drops of water and add 5 ml HF and evaporate to dryness on a hot plate. Allow to cool, rinse down the sides of the dish with a little water, add 5 ml of HClO₄ and again evaporate to dryness on a hot plate. (Repeat the evaporation with perchloric acid twice; second evaporations are not strictly necessary). Finally dissolve the residue in 3 ml HClO₄ and water. Transfer to a 50 ml volumetric flask and dilute to volume with water. Most of the silicate materials are dissolved with this treatment. If any residue remains, it must be collected and fused with potassium pyrosulphate (2 - 3 g). The melt is then dissolved in water containing a few drops of perchloric acid. This solution is added to the main solution and diluted to volume again (100 ml, if possible). Pipette a known volume (depending on the calcium and magnesium content) of the sample solution into a 100 ml volumetric flask, add 20 ml of lanthanum solution, dilute to volume with water and mix well.

Calibration: Prepare a set of standard solutions containing 0 - 50 μ g/ml of Ca and 0 - 6 μ g/ml of Mg, each with 20 ml of lanthanum solution in 100 ml volumetric flasks. Maximum care must be paid to the dilution process. Automatic pipettes are highly recommended.

Spray the sample and standard solutions into the air acetylene flame of the atomic absorption spectrophotometer using the appropriate lamp for Ca and Mg. With the present instrument, at least, two readings must be taken for each sample solution, each being preceded and followed by a reading on a standard solution, possibly of similar concentration. Distilled water can be used for the blank.

If the volume of the final solution is 25 or 50 ml, use 5 - 10 ml of lanthanum chloride solution.

The instrumental parameters used for atomic absorption determination of Ca and Mg are as follows:

Instrumental Parameters For:

	<u>Ca</u>	<u>Mg</u>
Lamp current	20 mA	4 mA
Wave length	427 nm	289 nm
Slid width	0.1 mm	0.005 mm
Burner elevator height	0.4 cm	0.8 cm
Air pressure	1.5 l/min	1.5 l/min
C ₂ H ₂ pressure	0.6 ml/min	0.6 ml/min

Two different calibration graphs have been obtained for Ca using normal and expanded scale, corresponding to concentration ranges from 0 to 50 $\mu\text{g/ml}$ and 0 -10 $\mu\text{g/ml}$ respectively. For samples containing less than 1 % of CaO the expanded scale must be used.

One calibration graph was used for Mg determination corresponding to a range of concentration from 0 to 6 $\mu\text{g/ml}$. To evaluate the limits of accuracy and precision achievable with the procedure described, two standard samples were analyzed for Ca and Mg in triplicate and replicate readings were run on the same solutions.

The results obtained were compared against the certificate values, as shown in Tab. 1. The results indicate that the described method can be used at the moment for determining CaO and MgO in silicate materials when the content is more than 1%.

The critical working conditions of the instrument are not suitable for samples containing less than 1%. The error in the case of glass sands will be so high that at the moment it is impossible to determine Ca and Mg in this kind of samples and achieve results within acceptable limits.

The bad performance characteristics of the instrument can be demonstrated by comparing the sensitivity obtained for Ca and Mg, with the corresponding values achievable with a double-beam Perkin Elmer spectrophotometer. The sensitivity expected for Mg and Ca respectively with a double-beam instrument is about 3 - 5 times better than the present values.

Correct results will be obtained for every kind of silicate materials, glass sands included, when a proper instrument and adequate means of dilution and standardization are used.

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B) DETERMINATION OF CaO AND MgO IN LIMESTONES

FINDINGS AND REMARKS

Brief outline of the existing method

- 0.5 g of sample is dissolved in 25 ml of HCl 5 %, by boiling.
- The total content of Ca and Mg is determined by EDTA titration at pH 10.
- Ca is determined by EDTA titration at pH 12-13, and Mg is calculated by difference.
- Eriochrome Black T is used as indicator and Triethanolamine as masking agent for Fe, Al and Mn.

The decomposition procedure used for limestones is correct. The EDTA titrimetric method is one of the best classical methods to determine Ca and Mg in carbonate materials. Nevertheless, it is not ideal for the determination of small quantities of Mg (and sometimes Ca) that occur in many carbonate rocks. The end point of the titration (especially for Mg) is not sufficiently sharp leading to highly inaccurate results. It is particularly sensitive to the presence of Mn and Fe making the end point difficult, if not impossible to detect. Even when triethanolamine is added as masking agent, it can be insufficient to eliminate this source of error. It would be preferable to remove Fe and Mn from the solution by a chloroform extraction of the metal b complexes with diethyl-dithiocarbonate. Some reagents solutions may decompose with time and must be freshly prepared at least every three days. This care is not commonly observed in the laboratory. The method is long. It takes about 4 hours to prepare the reagents and 1 - 1 ½ hours for a duplicate analysis, and requires many manipulations easily affected by operator errors. In short, the method is not suitable for routine analysis.

The accuracy of the method was checked by duplicate analyses on two samples containing different known concentrations of CaO and MgO. Since standard samples of limestone were not available, the samples were prepared by weighing and mixing spectopure reagents. The analytical results are reported in Tab. 3.

It appears that the EDTA method can be applied to determine Ca in high content carbonates, but gives inaccurate results for Mg, whatever the concentration may be. For low content of Mg the method cannot be used.

RECOMMENDATIONS

The atomic absorption method previously described for silicates analysis is applicable to the analysis of limestones provided that suitable equipment is used. The procedure is the same except for the decomposition method which is about the same used for EDTA method.

Decomposition method for limestones

Accurately weigh 0.5 g of finely ground (200 mesh) sample into a 125 ml beaker in duplicate. Add 25 ml of HCl 5 % and cover with a watch glass. Bring to the boil (10 minutes on a hot plate). Cool and transfer to a 50 ml volumetric flask washing the beaker and the watch glass. Dilute to volume and filtrate a small portion of the solution.

Pipette a given volume of the filtrate (depending on the content of the sample) into a 100 ml volumetric flask, add 20 ml of lanthanum solution. Dilute to volume with water and mix well. Proceed as described for silicate materials.

The method applied to the sample with known content of Ca and Mg has given the results listed in Tab. 4 and Tab. 5.

It can be observed that, despite the bad working conditions of the instrument, the method is generally preferable to the EDTA method (except for high content of Ca).

For Mg the results are more accurate in the whole range of concentration usually encountered in limestones. For Ca the method is less accurate than the EDTA method for samples with a high content of Ca, but also in this case the average percent error is under 6 %. For samples containing less than 10 % of CaO the average percent error is under 5 %, as shown in silicate analyses. Therefore, it is suggested to use the atomic absorption method from now on, also for limestones analysis of Ca and Mg, especially when quick results are requested. When the accuracy is more important than the speed, the EDTA method must be used only to determine Ca in samples containing more than 10 % CaO.

C) DETERMINATION OF Fe₂O₃

FINDINGS

The method of decomposition currently used in the laboratory is the same described above (in findings) for Ca and Mg determination in silicate. Fe is then determined by atomic absorption spectrophotometry without fixed operating conditions.

RECOMMENDATIONS

The following procedure is suggested: Determination of Fe by atomic absorption spectrophotometry.

Reagents

Stock Standard Solution

Iron 1000 $\mu\text{g/ml}$.: Dissolve 1,000 g of clean fresh iron in 50 ml of (1+ 1) HNO₃. Dilute to 1 litre with deionized water.

Procedure: The procedure is exactly the same suggested for Ca and Mg determination. For samples containing iron oxides or high content of iron, the fusion with 2.3 g of potassium pyrosulphate is necessary after acid attack.

Calibration: Prepare a set of standard solution containing 0 - 200 $\mu\text{g/ml}$ of Fe. For the atomic absorption measurements use the same procedure described for Ca and Mg, but the following operating conditions:

Instrumental Parameters for Fe

Lamp current	15 mA
Wave length	253 nm
Slit width	0.1 mm
Burner elevator height	1 cm
Air pressure	1.5 l/min
C ₂ H ₂ pressure	0.6 ml/min

This procedure was checked by determining iron in the same solutions of the two standard samples in which Ca and Mg were determined.

Two calibration graphs were used for two different concentration ranges (0-25 $\mu\text{g}/\text{ml}$ and 0 - 200 $\mu\text{g}/\text{ml}$) using normal and expanded scale (x 3) respectively.

The results are listed in Table 6 and are compared with the certificate values. Except for a few results most likely affected by the high fluctuation of the instrument, the percentage error is always under 6%. Therefore, the method can be used at the moment for the determination of iron in samples containing more than 1% and probably down to 0.5% Fe_2O_3 .

Using an adequate instrumentation and the right working procedures (dilution and standard solution) the method will be applicable to samples containing less than 0.5% down to 0.05% of Fe_2O_3 .

It is enough to say that the sensitivity and detection limits achievable with the usual double-beam spectrophotometer are about 10 times better than the values theoretically obtainable with the instrument employed.

D) DETERMINATION OF Na₂O AND K₂O

FINDINGS AND REMARKS

Brief outline of the existing method

0.4 g of sample is dissolved in 10 ml HF, 3 ml of H₂SO₄, digesting for one day on a steam bath. After cooling, the solution is evaporated down to about 3 ml and 1 ml of HNO₃ is added. The solution is then fumed to dryness and cooled. The residue is digested for 30 minutes with distilled water on a steam bath. The crucible is removed and washed with distilled water and the solution boiled to a volume \leq 150 ml. The solid residue is filtered off and the solution is made up to 200 ml.

Na and K are determined by flame photometer after proper dilution. The content of Na₂O and K₂O is calculated by comparison with respective calibration graphs obtained dissolving pure NaCl and KCl. The decomposition procedure is effective but it is not the best one for flame photometer where a nitric solution would be desirable.

The flame photometry and the atomic absorption spectrometry are practically the only methods used at present to determine Na and K. No other is as sensitive, accurate and precise.

The flame photometry is more sensitive than the atomic absorption spectrophotometry and is preferable when very low amounts of these elements must be determined. The following detection limits are likely to be obtained from a good flame photometer and a double-beam spectrophotometer:

	<u>Flame Photometry</u>	<u>AA Spectrophotometry</u>
Na	0.0001 p.p.m.	0.01 at 589 nm
K	0.001 p.p.m.	0.01 at 766.5 nm

Nevertheless, flame photometry is subject to several interference which must be taken into account, if accurate results are to be obtained.

- Spectrum interferences
- Radiation interferences due to emission by solvents and other elements
- High ionization extent of alkali metals that diminishes the proportion of atoms available for the transition which give rise to the resonance lines.

Some of these interferences can be avoided using atomic absorption spectrophotometry; some of them, such as radiation and high ionization, still remain. The effects can be minimized adding an ionization buffer, such as caesium sulphate and a radiation buffer, such as aluminium sulphate. To check on the accuracy and precision of the method used in the laboratory, Na and K were determined by flame photometry on the same solution of standard samples prepared for Ca and Mg. The measurements were made with either a normal scale or an expanded scale under the conditions currently used to determine Na and K. The results are reported in Tab. 7 and Tab. 8. It can be observed that the method can be used at the moment to determine Na and K in samples containing more than 1 % of Na_2O and K_2O , provided that repeated readings are made. It is preferable to use a normal scale.

For samples containing less than 0.5 % the results are completely inaccurate; therefore this technique is not suitable for the analysis of glass sands or similar materials. The high errors obtained in samples Sarm 6 are probably due to interference effects from other elements. To eliminate every kind of interference and lower the detection limit down to 0.01 %, the solution must be prepared following the procedure described later. The solution so prepared can be analysed by flame photometry or atomic absorption spectrophotometry. Good instruments obviously must be used. Indeed high instrument sensitivity is required for determining small amounts of alkali metals and this is well within the range of most modern instruments.

RECOMMENDATIONS

If other elements have to be determined in addition to sodium and potassium, the solution obtained by the decomposition method described for calcium and magnesium can be used. The procedure described in detail

in enclosure 9 is preferably adopted when Na and K only must be determined. Using the present flame photometer, weigh 0.2 - 0.5 depending on the content of the sample. The most sensitive emission wavelengths for sodium and potassium are 589.0 nm and 766.5 nm. An air-acetylene flame is recommended in atomic absorption spectrophotometry. The operating conditions will depend on the characteristics of the instrument used.

./.

E) DETERMINATION OF Al_2O_3

FINDINGS AND REMARKS

The following method is used in the laboratory to determine Al_2O_3 , either in silicate materials or in glass sands.

Brief outline of the existing method

0.2 g of sample is fused with 3 g of NaOH. The melt is dissolved in HNO_3 (1 : 2) and the solution is diluted to 500 ml. One aliquot of this solution is used for the colorimetric reaction with EDTA and Colochrome-cyanine. The color is read at 536 nm by comparison with a solution prepared in the same way but containing thioglycolic acid instead of EDTA.

Al_2O_3 content is determined by reference to a calibration graph.

The method applied to two standard samples has given the results shown in Tab. 9. It can be observed that the method as currently used gives inaccurate results either for high or for low content of Al_2O_3 . The colorimetric reaction was repeated on sample Sarm 2 by diluting the original solution (20 ml to 500 ml) and using 20 ml of this diluted solution.

The results reported in Tab. 10 show that this stage of dilution is absolutely necessary for samples containing more than 10 % of Al_2O_3 . In any case the method is unsuitable for samples containing less than 0.5 % Al_2O_3 , i.e., for glass sands.

RECOMMENDATIONS

The best method to determine Al_2O_3 whatever the content may be is the atomic absorption spectrophotometry, provided that an adequate instrument and a nitrous oxide-acetylene burner is used. The procedure described in detail in enclosure 10 and in the report later, is highly recommended.

The colorimetric procedure described in enclosure 11 can be used at the moment for high and low content samples. The results obtained by this method on the two standard samples (previously analysed with the EDTA Solochrome method) are reported in Tab. 11. As can be seen this method is more accurate and versatile than the EDTA method.

F) SiO₂ DETERMINATION

FINDINGS AND REMARKS

The classical gravimetric method is used to determine silica in every type of sample.

Brief outline of the existing method

0.5 g of the sample is fused with 6 g of Na₂CO₃. The melt is dissolved in diluted HCl (1 : 2) and the solution is evaporated to dryness. The residue is treated with 15 - 25 ml of HCl (sp.d.1.1). After diluting with an equal volume, filtration is done immediately and silica is washed. The filtrate and washings are evaporated to dryness. Precipitation of silica and evaporation of filtrate is repeated twice. The three residues are combined and ignited. The weighed residue is treated with HF and H₂SO₄. The loss of weight represents silica. In Tab. 12 the results obtained on two standard samples of silicate and on two samples of limestone with a known content of silica are reported. As can be seen, the method gives satisfactory results as regards accuracy, but it takes a long time (5 - 6 days) and is very tedious. Moreover, it is not suitable for silica contents under 2 - 1 %. The best method to determine SiO₂, whatever the content may be, is the atomic absorption technique previously recommended for aluminium and reported later. For the moment, especially when rapid results are requested, the colorimetric procedure described in the attachments is suggested. This procedure is much more rapid than the gravimetric method (4 hours generally are sufficient for the decomposition and colorimetric measurements of a series of samples) and gives results within acceptable limits.

In table 13 the results obtained on the two standard silicate samples previously analysed by the gravimetric method are reported. Standard limestone samples were not available to compare with the samples shown in Table 13, but certainly the accuracy would have been better than silicate samples for such low SiO₂ content. It is recommended to execute repeated readings in order to overcome the instability of the source intensity and the low effective transmission characteristics of the filter. The accuracy and precision of the method will be largely improved using an uv and a v spectrophotometer of the type previously recommended.

V. ANALYSIS OF SILICEOUS MATERIALS BY
ATOMIC ABSORPTION SPECTROPHOTOMETRY

The method is intended for the analysis of all types of inorganic siliceous materials decomposable by 38 - 40 % HF and containing, as main constituents, silicon, aluminium, iron, magnesium, calcium, sodium and potassium, and as additional components, titanium, manganese and chromium. In most cases, when all of the constituents listed are requested for the analysis, their determination can be incorporated in the present scheme. The method is based on the decomposition of a sample (normally 0.2 - 0.3 g) by HF (38 - 40 %) in a bomb under pressure. After the decomposition, boric acid solution is added to dissolve precipitate fluorides and the solution is diluted with water to a known volume (normally 100 ml). The atomic absorption measurements are made on the sample solution or an aliquot part taken from it.

SiO₂ and Al₂O₃ Determination

Reagents

Use standard solutions for atomic absorption spectroscopy. If standard solutions are not available, prepare the solutions in this way:

Silicon standard solution: 1 000 μ g/ml of silicon.: Ignite silicon dioxide to constant weight at 1 000 \pm 50° C. Weigh 0.2139 g and transfer to the decomposition vessel and proceed as described for sample decomposition. Transfer the solution to a 100 ml volumetric flask and dilute to volume with distilled water.

Aluminium standard solution: 1 000 μ g/ml of Aluminium: Dissolve 1.000 g of Al wire in a minimum of (1 +1) HCl, adding a small drop of mercury as a catalyst. Dilute to 1 litre with 1 % (v/v) HCl. Filter the solution to remove the mercury.

Decomposition vessel

The construction materials and the main features of the vessel used to decompose the sample by an acid mixture under pressure are illustrated in enclosure 10. A complete apparatus (bomb) has been delivered to the laboratory as specimen to be used to build new ones.

Procedure

Weigh 0.3000 g of the sample and transfer to the teflon crucible. Add 1 ml of aquaregia as a wetting agent, making certain that the sample has become thoroughly wetted. Then add 6 ml of concentrated HF and close the vessel by hand tightening the screw caps containing the teflon sealing disc. Place the crucible without tilting into a (drying) oven for 45 minutes at 140° C. Then let cool to ambient temperature. For some materials it is preferable to let the bomb overnight, as for samples with high content of Al₂O₃ (bauxites). Unscrew the lid and transfer the decomposed sample solution in a 250 ml beaker of teflon containing 5.6 of H₃BO₃ and 20 ml of H₂O. Wash thoroughly the sides of the crucible and the lid with the aid of about 10 ml of distilled water and transfer the washing waters into the beaker. Shake the beaker till complete dissolution of boric acid and precipitated metal fluorides. Transfer the solution to a 100 ml volumetric flask, adjust to volume and store in a polyethylene container. The sample solution should not remain in the glass container for longer than 2 hours. Dilute further with a glass pipette to volumetric flasks, if necessary. Aspirate the sample solution and the standards for silicon and aluminium into a nitrous oxide-acetylene flame. Determine aluminium at 309.3 nm and silicon at 251.6 nm. Use the operating parameters according to the instrument features. For a normal double beam instrument the sensitivity is about 1 µg/ml Al and about 1.8 µg/ml Si for 1 % absorption.

No matrix or interelement effects were observed with the new Perkin-Elmer models of the atomic absorption spectrophotometers (like 4 000 and 5 000 models).

VI. CONCLUSIONS AND RECOMMENDATIONS

FINDINGS

- The analytical methods currently used in the laboratory are mostly long traditional techniques (titrimetric, colorimetric and gravimetric) developed many years ago.
- Old and obsolete instruments, e.g. a single beam atomic absorption spectrophotometer Mod. S.P. 90 by UNICAM Ltd. and a flame photometer of Evans Electroselenium Ltd.) are occasionally used for some analyses.
- All these methods can give results within analytically acceptable limits for samples with middle and high content, but are generally unsuitable for samples containing less than 1 % of constituents.
- The skills of the technical personnel in the chemical laboratory are, on average, basically satisfactory.

RECOMMENDATIONS

- It is highly recommended to replace the existing methods with rapid instrumental techniques capable of guaranteeing accurate and precise results in a wide range of concentrations down to 0.1 - 0.01 % of constituents. In order to make the laboratory able to run routine analyses within the limits of time and accuracy requested by the geological and industrial activity.
- It is highly recommended to provide the chemical laboratory with adequate new instruments. They are listed here in order of importance:
 - a) Atomic absorption spectrophotometer; estimated cost 25 to 45,000 US \$
 - b) Ultra-violet and visible spectrophotometer; estimated cost 10 to 15,000 US \$
 - c) Flame photometer

- Training of the two senior laboratory staff is strongly recommended:
 - a) At the premises of the instrument suppliers, e.g. in operation and maintenance of the equipment.
 - b) In a functioning analytical laboratory which uses similar instrumental techniques for mineral and rock analyses.

- Further consultancy services are recommended for a period of about four months, such consultancy to follow installation, commissioning of the new equipment. Specifically, the consultant would:
 - a) Examine existing analytical methods which have not yet been checked in detail.
 - b) Examine analytical methods for future requirements.
 - c) Train laboratory staff in the operation of the new instruments, and adapt or fit the analytical requirements to the new instruments.

Table 1

Ca O Determination in silicates by atomic - absorption spectrophotometry

Sample	% CaO		Error	
	Certificate Value	Found	Absolute	Percent
Granite G.A.	2.5	2.58	+0.08	3.1
		2.45	-0.04	1.6
		2.43	-0.07	2.8
		2.71	+0.21	8.4
		2.60	+0.10	4.0
		2.63	+0.13	5.2
		2.52	+0.02	0.8
		2.59	+0.09	3.6
		2.41	-0.09	3.6
		2.52	+0.02	0.8
		2.59	+0.09	3.6
		2.37 Exp.	-0.13	5.2
		2.31 "	-0.19	7.6
SARM 3	3.3	3.22	-0.08	2.4
		3.48	+0.18	5.5
		3.11	-0.19	5.8
		3.50	+0.20	6.1
		3.35	+0.05	1.5
		3.13 Exp.	-0.17	5.2
		2.28 "	-1.02	30.9
SARM 6	0.31	0.20 Exp.	-0.11	55 ..
		0.23 "	-0.08	25 ..

Exp. = Expanded Scale

Table 2

Mg O Determination in silicates by atomic -
absorption spectrophotometry

Sample	% Mg O		Error	
	Certificate Value	Round	Absolute	Percent
Granite G.A	0.95	0.91	-0.04	4.4
		0.90	-0.05	5.3
		0.91	-0.04	4.4
		0.96	+0.01	1.1
		0.87	-0.08	8.4
		0.87	-0.08	8.4
		0.89	-0.06	6.3
		0.88	-0.07	7.4
SARM 3	0.36	0.24	-0.24	33.3 ..
		0.25	-0.11	30.6 ..
		0.25	-0.11	30.6 ..
		0.27	-0.09	25.0 ..
		0.26	-0.10	27.8 ..

Table 3

Determination of Ca O and Mg O by EDTA Method

Sample	(real) Present	% Ca O		Error		% Mg O		Error	
		Found	Absolute	Percent	(real) Percent	Found	Absolute	Percent	
N. 1	50	50.4	+0.4	0.8	0.5	0.0	-0.5	100	
		49.95	-0.05	0.1		0.1	-0.4	80	
N. 2	30	29.95	-0.05	0.16	20	17.3	-2.7	13.5	
		30.19	+0.19	0.63		18.1	-1.9	9.5	

Table 4

Ca O Determination in limestones by
atomic - absorption spectrophotometry

Sample	Present	% Ca O	Found	Absolute	Error	Percent
N. 1	50		49.56	-0.44		0.88
			54.32	+4.32		8.64 •
			51.80	+1.80		3.6
			49.80	-0.20		0.4
			50.68	+0.68		1.36
			50.92	+0.92		1.84
			54.84	+4.86		9.68 •
N. 2	30		29.68	-0.32		1.07
			31.78	+1.78		5.93
			27.14	-2.86		9.53 •
			29.94	-0.06		0.20
			28.08	-1.02		6.40
			30.08	+0.02		0.07
			28.09	-1.95		6.5

Table 5

Mg O Determination in limestones by atomic -
Absorption spectrophotometry

Sample	% Mg O		Error	
	Present	Found	Absolute	Present
N. 1	0.5	0.47	-0.03	6
		0.47	-0.03	6
		0.46	-0.04	8
		0.43	-0.07	14
		0.42	-0.08	16
		0.42	-0.08	16
		0.45	-0.05	10
		0.44	-0.06	12
		0.47	-0.03	6
		0.44	-0.06	12
		0.44	-0.06	12
N. 2	20	19.23	-0.77	3.85
		20.6	+0.6	3
		19.1	-0.9	4.5
		20.3	+0.3	1.5
		18.6	-1.4	7.0
		18.3	-1.7	8.5
		19.1	-0.9	4.5
		18.82	-1.18	5.9
		18.82	-1.18	5.0
		18.73	-1.27	6.35
		18.83	-1.17	5.85

TABLE 6

Fe₂O₃ determination by atomic -

- absorption spectrophotometry

Sample	% Fe ₂ O ₃		Error	
	certificate value	Found	Absolute	Percent
Granite GA	2.81	2.81	0.0	0
		2.86	+ 0.05	1.8
		2.86	+ 0.05	1.8
		2.86	+ 0.05	1.8
		2.65	- 0.16	5.7
		2.72	- 0.09	3.2
		2.86	+ 0.05	1.8
		2.75	- 0.06	2.1
		2.86	+ 0.05	1.8
		2.72	- 0.09	3.2
		2.87	+ 0.05	2.1
		2.77Exp	- 0.04	1.4
		2.66 "	- 0.15	5.3
		2.68 "	- 0.13	4.6
		2.69 "	- 0.12	4.3
		2.69 "	- 0.12	4.3
		2.80 "	- 0.01	0.4
		2.52 "	- 0.29	10.3
		2.77	- 0.04	1.4
		2.66 "	- 0.15	5.3
		2.66 "	- 0.15	5.3
		2.72 "	- 0.09	3.2
2.72 "	- 0.09	3.2		
2.66	- 0.15	5.3		
SARM 3	9.77	10.01	+0.24	2.5
		10.87	+ 1.1	11.3 ..
		9.01	- 0.76	7.8
		9.80	+ 0.03	0.3

Table 6 cont.

	9.87	+ 0.10	1.0
	8.65	- 1.12	11.5 ..
	9.30	- 0.47	4.8
	9.72	- 0.05	0.5
	10.37	+ 0.60	6.1
	10.08	+ 0.31	3.2
	8.22Exp	- 1.55	15.9 ..
	9.65 "	- 0.12	1.2

Exp = Expanded scale

Table 7

Na₂ O Determination by Flame Photometry

Sample	% Na ₂ O		Error	
	Certificate Value	Found	Absolute	Percent
Granite G.A.	3.6	3.37	+0.23	6.4
		3.77	+0.23	6.4
		3.77	+0.23	6.4
		3.77	+0.23	6.4
		3.34 Exp.	-0.26	7.2
		3.88 "	+0.22	7.8
		3.75 "	+0.15	4.2
		3.13 "	-0.47	13.1 .
		3.34 "	-0.26	7.2
		3.69 "	+0.09	2.5
		3.59 "	-0.01	0.3
SARM 3	8.27	7.95	-0.32	3.9
		8.49	+0.22	2.7
		7.82	-0.45	5.4
		8.36	+0.09	1.1
		6.87 Exp.	-1.40	16.9 .
		7.62 "	-0.65	7.9
		6.54 "	-1.73	20.9 .
		7.21 "	-1.14	13.8 .
SARM 6	0.1	0.03 Exp.	-0.07	70 ..
		0.03 "	-0.07	70 ..

Exp. = Expanded Scale

Table 8

K₂ O Determination by Flame Photometry

Sample	% K ₂ O		Error	
	Certificate Value	Found	Absolute	Percent
Granite G.A.	4.05	4.03	-0.02	0.49
		4.07	+0.02	0.49
		3.87	-0.18	4.4
		4.22	+0.17	4.2
		3.95	-0.10	2.5
		3.74 Exp.	-0.31	7.7
		4.03 "	-0.02	0.49
		4.12 "	+0.07	1.7
		3.98 "	-0.07	1.7
SARM 3	5.54	5.23	-0.31	5.6
		5.42	-0.12	2.1
		4.70	-0.84	15.2 .
		4.53	-1.01	18.2 .
		4.94	-0.6	10.8 .
		5.12	-0.42	7.6
		4.52 Exp.	-1.02	18.4 .
		5.18 "	-0.36	6.5
		4.58 "	-0.96	17.3 .
		4.94 "	-0.60	10.8
SARM 6	0.016	0.0085 Exp.	-0.0075	46.9 ..
		0.0084 "	-0.0076	47.5 ..

Exp. = Expanded Scale

Table 9

Al₂O₃ Determination by EDTA- Solochrome cyanine method currently used

Sample	% Al ₂ O ₃ Certificate value	Found	Error	
			Absolute	Percent
SARM 2	17.33	14.4	-2.93	16.9
"		14.2	-3.13	18.1
SARM 6	0.44	0.4	-0.04	9.1
		0.3	-0.14	31.8

Table 10

Al₂O₃ Determination by EDTA-Solochrome - Cyanine method using previous dilution

Sample	Certificate value	% Al ₂ O ₃ Found	Error	
			Absolute	Percent
SARM 2	17.33	17.7	+0.37	2.14
		17.7	+0.37	2.14

Table 11

Al₂O₃ Determination as
Calcium - Alizarin Red-S Complex

Sample	% Al ₂ O ₃		Error	
	Certificate Value	Found	Absolute	Percent
Sarn 2	17.33	17.30	-0.03	0.17
		17.21	-0.12	0.69
Sarn 6	0.44	0.45	+0.01	2.27
		0.45	+0.01	2.27

Table 12

SiO₂ Determination by Gravimetric method

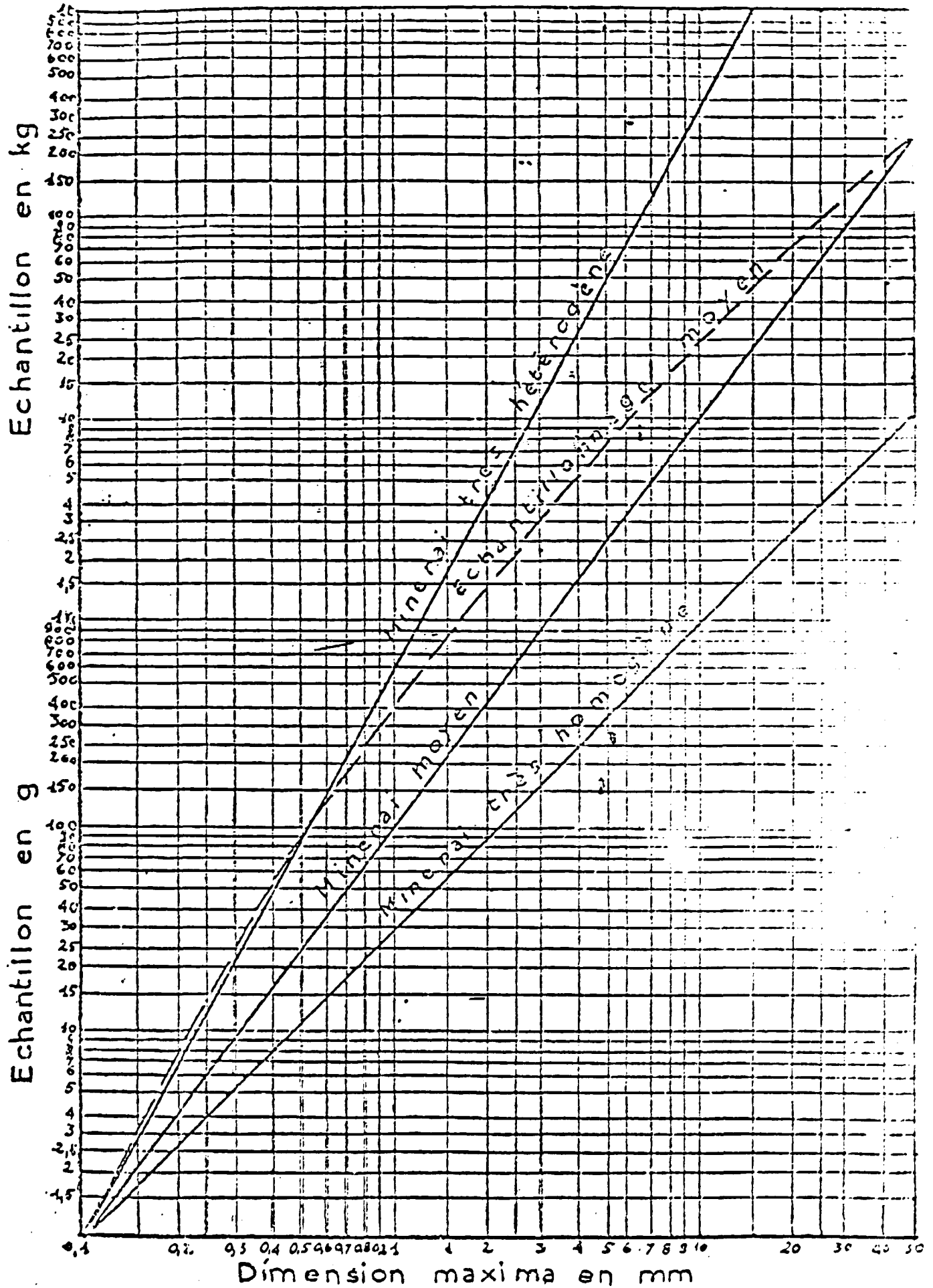
Sample	% SiO ₂		Error	
	Present	Found	Absolute	Percent
SARM 2	63.72	63.0	-0.72	1.13
		62.5	-1.22	1.91
SARM 6	38.86	38.6	-0.26	0.67
		38.3	-0.56	1.44
Limestone 1	10.20	10.1	-0.10	0.98
		9.8	-0.40	3.92
Limestone 2	26.45	25.5	-0.95	3.59
		25.1	-1.35	5.10

Table 13

SiO₂ Determination by Molybdenum blue method

Sample	Certificate Value	%SiO ₂		Error	
		Found	Absolute	Percent	
Sarm 2	63.72	62.5	-1.22	1.9	
		62.5	-1.22	1.9	
		60.5	-3.22	5.1	
		60.3	-3.42	5.3	
Sarm 6	38.86	39.6	+0.66	1.6	
		40.2	+1.36	3.1	
		37.4	-1.46	3.8	
		37.4	-1.46	3.8	

DIAGRAMME D'ECHANTILLONNAGE



IMP. PAUL ET FÉLIX

