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ANALYSIS OF ROCKS AND MINERALS BY
ATOMIC ABSORPTION SPECTROSCOPY
PART 3. A LITHIUM-FLUOBORATE SCHEME
FOR SEVEN MAJOR ELEMENTS

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DEPARTMENT OF ENERGY, MINES AND RESOURCES

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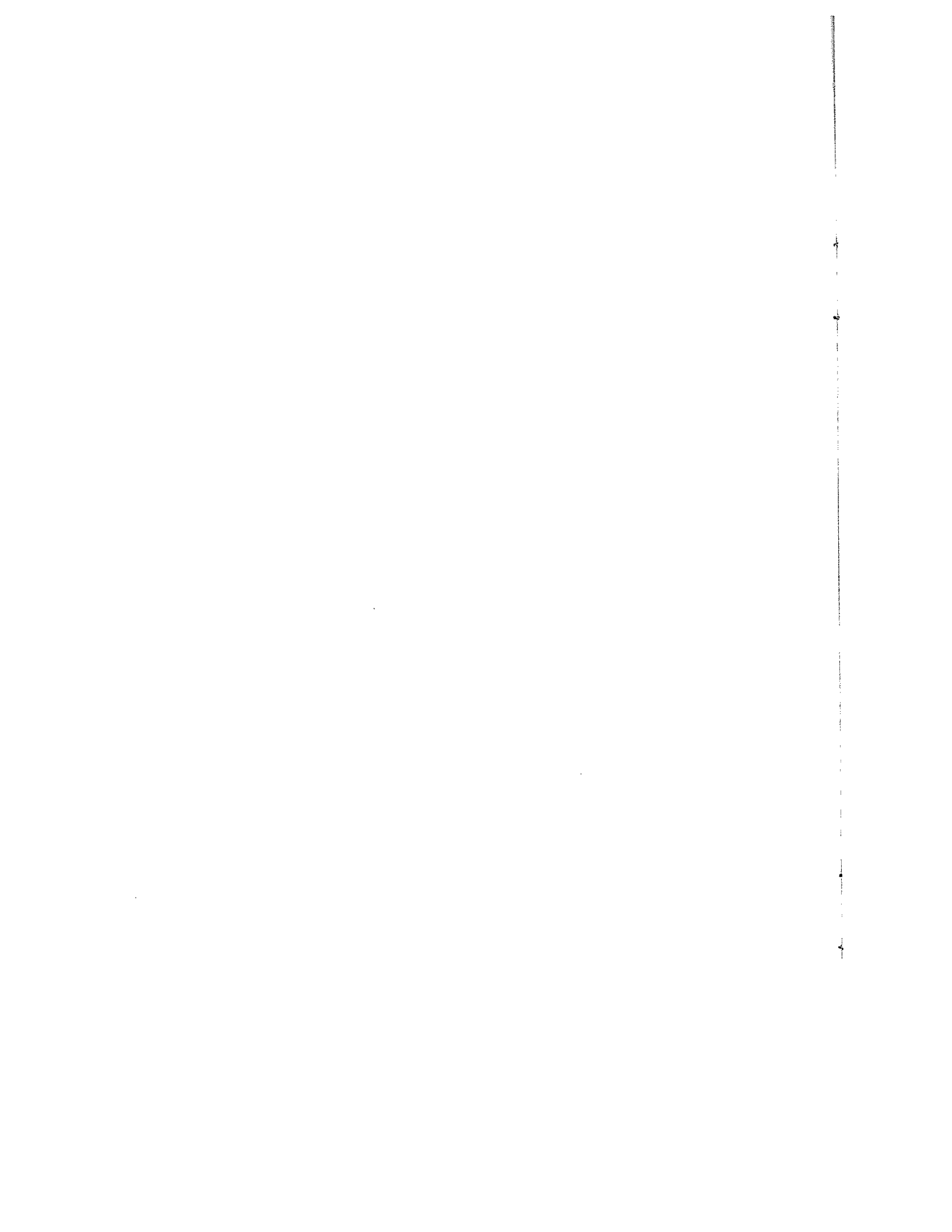
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ABSTRACT

A new analytical scheme is proposed, whereby silica, alumina, total iron, magnesium, calcium, sodium and potassium are determined in silicate rocks and minerals by atomic absorption spectroscopy. Samples are decomposed by fusion with lithium metaborate, the fusion is dissolved in dilute hydrofluoric acid, and excess fluoride is complexed by the addition of boric acid. The resulting stable solution contains all of the nonvolatile components of the sample, and aliquots are analyzed by comparison with solutions similarly prepared from international reference samples of rocks. Possible extension of the method to other components is discussed.

RÉSUMÉ

On propose un nouveau schéma analytique pour le dosage de la silice, de l'alumina, du fer entier, du magnésium, du calcium, du sodium et du potassium dans les roches et minéraux silicatés par la spectroscopie d'absorption atomique. On décompose les échantillons par fusion au moyen du métaborate de lithium, on dissout la fusion dans de l'acide fluorhydrique dilué et on ajoute de l'acide borique pour faire des complexes avec le surplus de fluorure. La solution stable qui est produite comprend tous les composants nonvolatiles de l'échantillon, et on peut analyser des aliquots en les comparant avec de telles solutions, préparées avec des échantillons étalons internationaux. On discute les possibilités d'adapter cette méthode à d'autres éléments.



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INTRODUCTION

Earlier papers (Abbey, 1967, 1968) outlined the principles of atomic absorption spectroscopy, its application to the determination of certain major and minor elements in silicate rocks, and the development of a composite scheme for the determination of five major components using the same sample solution. The composite scheme involved both economy of sample and good precision and accuracy. The five elements (total iron, magnesium, calcium, sodium and potassium) can be determined in the same solution of most samples with the consumption of only a few milligrams of sample, and with an accuracy approaching (in some cases exceeding) that of conventional analysis.

As an attempt to simplify a proposed general analytical scheme combining atomic absorption with conventional methods, development of a method for determination of aluminum was then undertaken. It soon became apparent that the sample solutions prepared for the determination of the five other elements were not suitable. Subsequent work led to a scheme involving an entirely new approach to the problem of sample dissolution - i.e. fusion in lithium metaborate, followed by dissolution in hydrofluoric and boric acids. The solutions thus produced have been found suitable for the determination of silica and alumina, as well as the five other major elements listed above. Although no development work has been done, it is possible that the same solution (with further treatment in some cases) will be suitable for the determination of manganese, phosphorus, titanium, barium, strontium, chromium, etc., using atomic absorption and colorimetry.

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SAMPLE DECOMPOSITION TECHNIQUES

Traditionally, silicate rock and mineral samples have been decomposed for analysis by variants of two different procedures. In one, the sample is decomposed by fusion with an alkaline flux (generally sodium carbonate), followed by acidification and dehydration. In the other, the sample is dissolved by the action of hydrofluoric acid (generally in the presence of another acid). The major difference between the solutions resulting from the two procedures is that one essentially precipitates the silica, whereas the other volatilizes it. Further, the fusion procedure is not suitable for determination of the alkali metals because of the large amount of alkali metal (generally sodium) added in the flux.

Thus neither of the older established methods produces a stable solution which contains the silica along with all other nonvolatile components. Further, neither method is completely effective in decomposing certain resistant minerals, such as zircon, chromite, tourmaline, etc.

The lithium metaborate fusion method was first applied in silicate analysis by Ingamells (1964, 1966) and by Suhr and Ingamells (1966). The method is very effective in decomposing resistant minerals, yielding a fusion product which readily dissolves in dilute nitric acid, and which contains the silica and all of the other nonvolatile components of the sample. Many variants of the method have appeared in the literature. Thus some analysts have done the fusion in graphite, others in platinum crucibles; some have substituted lithium tetraborate or a mixture of lithium carbonate and boric acid for the lithium metaborate; and some have substituted hydrochloric or citric acid for nitric to dissolve the fusion product (Ingamells, 1964, 1966; MacKay, pers. comm., 1969; Govindaraju, 1966; Shapiro, 1967).

There has been considerable difference of opinion regarding the stability of the silica in solutions produced by such operations. Ingamells (pers. comm., 1968) claims that silica can be determined accurately even after the dilute nitric acid solution of a metaborate fusion has been left standing for some months, but Medlin, Suhr and Bodkin (1969) recommend that silica be determined as soon as possible after the solution is prepared (by essentially the same procedure as that used by Ingamells).

A novel approach to sample decomposition for comprehensive analysis of rocks was introduced by Langmyhr and Graff (1965). They decomposed the sample in a Teflon-lined pressure vessel by the action of hydrofluoric acid alone, and subsequently masked the excess fluoride by the addition of an excess of aluminum chloride. Silica was determined on the resulting solution by the molybdenum blue reaction. A separate solution was prepared by the conventional hydrofluoric-sulphuric acid treatment for the determination of the other nonvolatile components by various methods.

Subsequently, Langmyhr and Paus (1968) improved the method by using boric acid instead of aluminum chloride to mask the excess fluoride. The resulting solution was probably not suitable for analysis by some photometric methods, but was used successfully for the determination of silica and most of the other nonvolatile components by means of atomic absorption spectroscopy. The scheme was also applied to other types of materials which contain silica. Bernas (1968) used a similar system, and established experimentally the minimum quantity of boric acid required to provide a solution which may be stored in glass for up to two hours without measurable silica contamination.

Two other novel schemes have been proposed. Katz (1967) used a sodium hydroxide fusion, essentially that used by Shapiro and Brannock (1962) for photometric determination of silica and alumina, to produce a solution for the determination of the same elements by atomic absorption. His results showed some systematic errors. Galle (1968) decomposed silicate samples by means of hydrofluoric and sulphuric acids, evaporated the solutions to dryness and used potassium pyrosulphate to fuse the residue, thereby assuring complete solution of alumina and titania. The resulting solution was then analyzed by atomic absorption for many components, but silica was lost and the alkali metals could not be determined.

STANDARD SOLUTIONS

Many standard solutions are required for the quantitative determination of the major components of silicates by atomic absorption. If separate standard solutions are prepared for each component, and if varied rock types are to be analyzed, the number of standard solutions can easily exceed 100, with the attendant tedious preparations, storage problems and uncertain stability.

The standard solution preparation problem was partially simplified (Abbey, 1968) by preparing "standard blends", which could be used to determine several different elements. The procedure had the further advantage of permitting the preparation of standard solutions which were similar in general composition to the sample solutions, and were also useful in simplifying the study of inter-element interference. However, the scheme still involved many tedious measurements with pipettes and a microburette, with many opportunities for error.

In developing a scheme of analysis which includes silica with other major and minor elements, it appeared virtually impossible to ensure similarity in chemical composition and history between blended standard solutions and sample solutions. A plausible alternative would be the use of "standard rocks", which could be dissolved by the same procedure as used with the samples, thereby assuring chemical similarity between samples and standards.

Of the increasing number of international reference samples of rocks now available, the largest amount of analytical data has been published on the two granites and a basalt (GA, GH and BR) issued by the Centre de Recherches Pétrographiques et Géochimiques, Nancy, France, and on the granite, granodiorite, andesite, basalt, peridotite and dunite (G-2, GSP-1, AGV-1, BCR-1, PCC-1, and DTS-1) issued by the U.S. Geological Survey, Washington. Tentative "recommended values" for the French samples were given by Roubault, de la Roche and Govindaraju (1966). Revised values were given by Govindaraju (pers. comm., 1969). Flanagan (1969) reported a lengthy compilation of data on the American samples, but gave no recommended values. Abbey (in press) described an empirical scheme for deriving usable "proposed values" for the six American samples.

The nine samples represent a wide range of compositions for all components. In practice, compositional gaps can be filled by mixing solutions of individual reference samples. The range of percentages for any element can be extended by adding small amounts of a concentrated standard solution of that element to an aliquot of a solution of a reference sample without greatly affecting the overall chemical composition.

APPARATUS

Most of the equipment used has been described earlier (Abbey, 1968). For the present work, ASL shielded-cathode hollow-cathode lamps were used for silica, calcium and magnesium (a two-element lamp) and iron. Conventional hollow-cathode lamps were used for aluminum, sodium and potassium. Where a shielded hollow-cathode lamp was substituted for an older conventional lamp, it was generally necessary to change the operating current and slit width. Instability in an argon-filled calcium-magnesium lamp was overcome by switching to a neon-filled lamp.

A variable-flow nebulizer was used with the Techtron AA-3 atomic absorption instrument. That component proved useful not so much to vary sample uptake rates as to readjust uptake to a fixed value following uncontrolled changes, probably resulting from slight corrosion effects. An uptake rate of 4 ml per minute was adopted as standard.

Some readings were taken on a Techtron AA-5 instrument, whose more stable read-out module proved advantageous for silica. Unfortunately the advantage was largely offset by an excessive uptake rate, resulting in a too rapid build-up of salt residues in the burner. An AA-5 equipped with a variable flow nebulizer would probably be superior.

A flat-top burner head with a 5-cm slot was used at first for the acetylene-nitrous oxide flame. Excessive carbon build-up was observed with the fuel-rich flames required for silicon and aluminum. The difficulty was largely overcome by changing to the grooved titanium burner head, which has a 6-cm slot.

Difficulties with the Hamamatsu R-213 photomultiplier tube in the red end of the spectrum where potassium is determined (Abbey, 1968) were eliminated by changing to another R-213, specially selected for red sensitivity.

EXPERIMENTAL

It was decided not to use the method involving decomposition by hydrofluoric acid under pressure, for two reasons: (a) certain resistant minerals may not be decomposed, and (b) the pressure vessel does not lend itself readily to simultaneous decomposition of several samples, particularly in relatively unskilled hands. Similarly, the various schemes involving fusion with lithium borates followed by solution in dilute nitric or hydrochloric acids, were not considered suitable because of the questionable stability of silica in the resulting solutions. If standard solutions are to be prepared from reference samples, it is important that solution stability in terms of all components of interest should be as high as possible.

Some attempts were made to use the free acid form of ethylenediamine-tetracetic acid to dissolve the lithium metaborate fusion product, as suggested by Govindaraju (pers. comm., 1968), but it was not possible to obtain a clear solution at all times.

It was then decided to combine the best features of the lithium metaborate fusion and the hydrofluoric-boric acid system. The former has the advantage of readily decomposing resistant minerals. The latter appears to produce more stable solutions, in which such elements as silicon, aluminum, ferric iron and titanium exist in the form of fluo-anions; excess fluoride

is held in the form of fluoborate, and excess borate exists as the orthoborate ion. Bernas (1968) reports that fluoboric acid undergoes stepwise hydrolysis, eventually producing hydrofluoric and boric acids. The other fluoanions may decompose similarly. However, Paus (pers. comm., 1968) claims that there is no change in the apparent silicon content determined by atomic absorption after the solution has stood for six months in a fluoborate solution. Limited experiments in this laboratory have tended to support Paus' claim.

In the procedure now proposed, the sample is fused with a five-fold excess of lithium metaborate. The cooled fusion is dissolved in dilute hydrofluoric acid, followed by the addition of boric acid to complex the excess fluoride ion and to dissolve any precipitated fluorides. The quantities of reagents used are such as to produce final fluorine and boron contents corresponding to those recommended by Bernas for the preparation of solutions which are stable toward glass containers for at least two hours. If such solutions are stored in tightly-capped polyethylene bottles, they appear to be almost indefinitely stable in terms of the atomic absorption characteristics of the principal elements. Presumably because there is no glass surface with which hydrofluoric acid can react, and no opportunity for that volatile acid to escape, the resulting equilibrium produces a solution of sufficient stability.

Reagent Problems

Several batches of "lithium metaborate" received from a reputable manufacturer showed anomalous behaviour - i.e. unfused material effervesced when treated with acid, and fusion resulted in weight loss. Inasmuch as lithium metaborate is produced by interacting lithium carbonate with boric acid, it was assumed that the reaction, in this case, had not gone to completion. However, some workers prefer a lithium carbonate-boric acid mixture (Govindaraju, 1966; Omang, 1969), so such "defective" material may actually be quite suitable. Others have emphasized the need to purify lithium borate (e.g. Ingamells, 1966). Fortunately, a sufficiently pure grade of true lithium metaborate is now available commercially from at least one source.

The strontium carbonate used to prepare the strontium solution used in the earlier methods (Abbey, 1967, 1968) was sufficiently free of the elements to be determined. Unfortunately, when the supply of 1962 material then used became exhausted, it was found that similar material, obtained from the same and other manufacturers, contained too much calcium for our use. On the other hand, strontium nitrate was found to be satisfactory. For use with the new lithium fluoborate scheme, it may be simply dissolved in water. For use with the older acid decomposition, the strontium nitrate is converted to chloride by boiling and evaporating a solution of the nitrate with hydrochloric acid.

Interference Effects

In the earlier method (Abbey, 1967, 1968), strontium was used as a universal buffer, serving as releasing agent, ionization suppressor and to eliminate other less explicable interelement effects. The new system introduced two complicating factors: (a) the presence of silica in the solution

could lead to increased "chemical" interference in the air-acetylene flame, and (b) increased ionization effects may be expected in the hotter acetylene-nitrous oxide flame.

To examine these effects, calcium and magnesium absorptions were measured, using solutions derived from the lithium fluoborate treatment of samples of typical rocks. With the air-acetylene flame, it was found that no additional strontium was required, to release calcium and magnesium from the effect of silica, than was required to release them from the effect of aluminum in solutions derived from the hydrofluoric-perchloric acid decomposition. In the nitrous oxide-acetylene flame, neither calcium nor magnesium required a releasing agent. However, calcium is subject to ionization effects in that flame. Strontium addition was used to overcome such effects, 3,000 ppm Sr being found sufficient to repress the ionization of the equivalent of 0.5 per cent CaO in a fluoborate solution containing 50 mg of sample in 100 ml. Because of increased sensitivity in the nitrous oxide flame, it is advisable to determine CaO, where less than one per cent is present in the sample, by means of that flame.

Magnesium behaved very differently from calcium in the nitrous oxide flame. Sensitivity was actually inferior to that in the air acetylene flame, whereas the addition of varying amounts of strontium had no noticeable effect.

Aluminum is known to be subject to ionization effects in the nitrous oxide flame, and potassium is usually added to suppress the ionization. However, it was found that 3,000 ppm Sr was adequate for the purpose in dealing with the quantities of alumina normally found in a rock, with 50 mg of sample in 100 ml of a lithium fluoborate solution.

For silica determination, the addition of strontium was not found to be necessary, but a slight increase in silica sensitivity was observed when strontium was present.

The fact that no additional strontium was required to release calcium and magnesium from the chemical interference of silica in a fluoborate solution in the air-acetylene flame, tends to confirm the statement by Bernas (1968) regarding the fluoborate system's "... ability to compensate for inter-element effects and thus eliminate interference phenomena ...". A possible explanation may be found in the suggestion by Sastri, Chakrabarti and Willis (1969) that chemical interference in the flame, generally attributed to the formation of "inter-oxide" compounds (e.g. magnesium aluminate, calcium silicate, etc.), actually is the result of metal-oxygen bonds in the sample solution. In a fluoborate solution, the fact that such interfering elements as aluminum and silica are bound to fluorine would tend to diminish chemical interference. The chemical interference due to sulphate and phosphate would probably not be eliminated in a fluoborate system. Although the sulphur and phosphorus contents of most rocks are too low to have any effect, it would be necessary to check such effects if the fluoborate scheme were extended to phosphate rocks or to materials rich in sulphur.

Operating Parameters

As a result of the above interference and sensitivity tests, the following scheme was adopted: A 200-mg sample is dissolved and the solution made up to 200 ml. An aliquot containing 50 mg of sample is diluted to 100 ml, with strontium added to give a final concentration of 3,000 ppm Sr. That

solution is used to determine silica, alumina and very low calcium contents with the nitrous oxide flame. It may also be used to determine low potassium contents with the air-acetylene flame (see Table I).

Another aliquot, containing 10 mg of sample and sufficient strontium to give 1,500 ppm in the final solution, is also diluted to 100 ml. It may be used to determine ordinary quantities of iron, magnesium, calcium, sodium and potassium with the air-acetylene flame. Moderately small amounts of calcium may also be determined in this solution, using the nitrous oxide flame (see Table I).

For all elements, the working range of concentration may be extended upward by rotating the burner head. However, for MgO contents exceeding 15 per cent, smaller aliquots, containing 5 or 2 mg of sample, are necessary. The strontium content of such solutions is held at 1,500 ppm.

The operating parameters are given in detail in Table I. It will be seen that all concentrations (except that of the strontium buffer) are expressed in terms of percentage in the sample, not ppm in the solution. This is possible because reference samples are used as standards, and they are decomposed and diluted in exactly the same manner as are the samples for analysis.

Tests With Reference Samples

In order to confirm the suitability of the reference samples for preparation of standard solutions, each was analyzed for the five elements covered by the older method (Abbey, 1968). Samples of all were decomposed by the hydrofluoric-perchloric acid treatment, and suitable aliquots taken for the various determinations. For all five elements, each sample was taken in turn as an "unknown", and each element determined by atomic absorption, the sample being bracketed between two other samples (used here as "standards") containing a little more and a little less of the element contained in the "unknown". Where too great a gap was involved, or where the sample containing the largest amount of a given element was being analyzed, a measured amount of a standard solution of the element was added to the "low" standard. Where the sample containing the smallest amount of an element was being analyzed, the "low" standard was an aliquot of a blank that had been carried through the sample preparation procedure. In some cases, the desired concentration of an element in a standard solution was attained by mixing aliquots of the concentrated solutions of two different reference samples, or of a reference sample and the blank.

By using such a scheme, it was possible to verify the validity of the method without detailed studies of all the possible inter-element effects. Thus in determining, say, MgO, in sample A, using samples B and C as "high" and "low" standards respectively, a good result for MgO in A would show that the relatively random amounts of all of the other elements in the three samples have exerted no measurable effect on the result. Similar results on all of the available reference samples would confirm that no compensating errors were occurring. In analyzing samples, there would be no danger of encountering inter-element effects, except where some element was present in amounts outside the range covered by the reference samples. In that case, a check on the effect of the unusual component would be required.

The entire set of tests was then repeated, using sample solutions prepared by the lithium fluoborate method, and extending the elements determined to include aluminum and silicon. A standard solution of silicon was

prepared, for use in adding small amounts of silicon where required, by treating a small aliquot of a gravimetrically standardized, stabilized colloidal suspension of silica with hydrofluoric acid and boric acid, with the final concentrations of fluorine and boron adjusted to correspond to those in the sample solutions. Similarly, a standard titanium solution was prepared by fusing pure titanium dioxide with lithium metaborate and continuing with additions of hydrofluoric and boric acids, as with sample solutions.

Results of the tests done by both methods are compared with proposed or recommended values for the various reference samples in Table II.

DISCUSSION

With few exceptions, the results for iron, magnesium, calcium, sodium and potassium are as close to the recommended or proposed values in the reference rocks as would be expected in a precise analysis. Results for alumina are not quite as good as those for the five elements listed above, but would probably be considered almost acceptable for precise work. With those samples which contain relatively little alumina (PCC-1 and DTS-1), results by the proposed method are probably better than what would be expected from conventional methods, unless provision is made for the removal of iron and titanium.

The silica results are somewhat disappointing. They are probably better than those attainable by so-called "rapid" methods, but not good enough for really precise analysis. Possibly, some improvement in silica values might be attained by changing the sample concentration or that of the additives. However, the method would then lose the advantage of simplicity.

It is proposed to study the possibility of determining additional elements in the same two dilutions of the master sample solution that now serve for the determination of seven elements, with modifications if necessary. Two possibilities are titanium and manganese, although sensitivity limitations may restrict the usable range of concentrations for those elements. Chromium, barium and strontium are other possibilities, where they are present in sufficient quantity. Although simple colorimetric methods are available for some of these elements, much less sample solution would probably be required in atomic absorption.

It may be possible to determine phosphorus colorimetrically by the heteropoly blue method, using the same solution, because fluoride and borate ions reportedly do not interfere (Boltz, 1958).

It is not likely that trace elements in rocks can be included in the proposed scheme, because the sample solutions used are not sufficiently concentrated. That difficulty might be overcome by using more concentrated solutions, but new problems may then arise with salt build-up in the burner. Another interesting possibility would be to use flame emission instead of atomic absorption. Fassel (1969) claims that flame emission has many advantages, but it would require a wavelength scanning system to correct for background emission. Emission measurements would likely be superior in the case of rubidium and cesium, and possibly for the rare-earths.

ADDENDUM

After this manuscript had been completed, experiments conducted by J. L. Bouvier and the author indicated that manganese (0.01-1.00 per cent MnO) and chromium (0.01-1.00 per cent Cr₂O₃) may be determined on the solution containing 50 mg of sample in 100 ml, using the air-acetylene flame. Attempts to determine titanium by atomic absorption, using the nitrous oxide-acetylene flame, indicated that a higher sample concentration would be required. However, titanium may be readily determined photometrically with the Tiron reagent, using another aliquot of the master sample solution. Prior removal of silicon, boron and fluorine is then required, and this is accomplished by adding more hydrofluoric acid and some sulphuric acid, followed by repeated evaporation to sulphur trioxide fumes. Phosphorus may also be determined as molybdenum blue, using still another aliquot of the master sample solution. Removal of silicon, boron and fluorine is not required before phosphorus determination.

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APPENDICES I-III



APPENDIX I

Preparation of Standard Solutions

Both sets of metal standard solutions (at the 1,000 ppm and 100 ppm oxides level), described in Part 2 (Abbey, 1968) are required for use with the acid-decomposition procedure (APPENDIX II) and the lithium fluoborate system (APPENDIX III). However, to prepare the standard titanium solution for the lithium fluoborate system, it is better to take 200 mg of reagent grade TiO_2 through the normal sample dissolution procedure in APPENDIX III and to dilute to a final volume of 200 ml, giving 1,000 ppm TiO_2 in a lithium fluoborate matrix.

In addition, for the lithium fluoborate system, it is necessary to prepare a standard silica solution (at the 1,000 ppm SiO_2 level) by mixing a measured volume of a diluted, gravimetrically standardized, stabilized colloidal silica suspension with 30 ml of concentrated HF in a transparent plastic vial (Dupont 'Ludox' was used in this work, enough being taken to contain 1g of SiO_2). Cover the vial and stir magnetically until a clear solution is obtained. Pour the solution into a 600-ml polypropylene beaker containing 30 g of boric acid crystals. Add 200-300 ml of water and stir magnetically to dissolve the boric acid. Dilute to 1 litre in a volumetric flask and transfer to a polyethylene bottle.

Because the above solutions are used only to make small additions to solutions prepared from "standard" rock samples, they need not be standardized as accurately as would be necessary if they were used to prepare "standard blends", as in Part 2.

To prepare the main standard solutions, decompose the nine international reference samples listed in Table III by exactly the same procedure as used with samples for analysis. The additional standards used - AGV-GSP, BCR-BR, and BR-PCC - are blends prepared from AGV-1, GSP-1, BCR-1, BR and PCC-1. For the 50 mg per 100 ml level, that means mixing 25-ml aliquots of the master solutions of the two samples; for the 10 mg per 100 ml level, 5-ml aliquots of each. These blends serve to bridge several gaps in the compositions of the reference samples. To analyze samples containing more of one component than is present in any standard, sufficient standard solution of that element is added to an aliquot of the solution of the reference sample containing the maximum amount of that element, thereby providing "high" and "low" standards to bracket the sample. For samples containing less of one component than is present in any standard, a blank solution can serve as "low" standard.

Table III lists the values used for the reference samples in this work, based on Govindaraju (pers. comm.) and Abbey (in press). The table includes values for titanium, manganese, barium, strontium, chromium and nickel, because it may be possible to determine those elements by an extension of the proposed method, with modifications if necessary.

For general analytical work, solutions of the nine reference samples should be prepared at the start. If one reference sample is taken through the decomposition procedure with each lot of samples for analysis, then all of the reference sample solutions can be renewed in rotation. Where required by the nature of the samples being analyzed, the rotation scheme can be concentrated on a selected few reference samples.

APPENDIX II

Acid Decomposition Method

This method is used where silica and alumina determinations are not required. The procedure is the same as that outlined in Part 2, except that standard solutions are prepared by decomposing international reference samples.

The strontium solution for this method, formerly prepared from strontium carbonate, should be prepared from strontium nitrate as follows:

Weigh 72 g strontium nitrate into a 1-litre beaker and dissolve in about 150 ml of water. Add 225 ml concentrated HCl and boil until colourless. Evaporate to dryness on a steam bath. Redissolve in water and 200 ml of concentrated HCl, dilute to 2 litres in a volumetric flask and transfer to a polyethylene bottle. The solution then contains 15,000 ppm of Sr in 1.2 N HCl.

APPENDIX III

Lithium Fluoborate Method

Special Reagents

1. HF (1:9)
2. Boric Acid, 50 g per l.
Heat 600 ml of water to boiling in a 1-litre beaker containing a Teflon-coated stirring bar, on a magnetic stirrer-hot plate. Add 100 g of boric acid crystals and stir to dissolve while heating. Pour the solution into about 1 litre of cold water in a 2-litre beaker. Stir, dilute to 2 litres and store in a polyethylene bottle.
3. Strontium Nitrate, 15,000 ppm Sr.
Dissolve 72 g strontium nitrate in about 1 litre of water and dilute to 2 litres. Store in a polyethylene bottle.
4. Standard Solutions
See APPENDIX I
5. Blank Solutions
Prepare a master blank solution by dissolving 1 g of lithium metaborate in 60 ml HF (1:9) in a plastic beaker and continue as with samples (do not do a blank fusion). For each size of aliquot used in analysis, prepare a corresponding blank, where required, using a similar aliquot of the master blank solution.

Sample Treatment

Weigh 0.2 g of sample (correct to 0.1 mg) into a small porcelain crucible. Place in a muffle furnace, cover and move cover slightly aside. With furnace door slightly open, ignite at 550-600°C, preferably over night.

Remove from furnace and allow to cool.

Weigh 1 g lithium metaborate into a 30-ml platinum crucible. Add the cooled sample and mix well with a glass rod.

Cover the crucible, place in a muffle furnace and raise temperature to 950-1000°C. Hold at that temperature for 15 minutes, remove the hot crucible and rotate it to spread the fusion over the walls. When the fusion has solidified, return the crucibles to the furnace (reversing the order if samples are being run in a group) and heat 5 minutes more after reaching 950-1000°C.

Place 25 ml in a 250-ml polypropylene beaker. Remove crucible from furnace, rotate it to spread the fusion and quench the crucible in the water, leaving it upright in the beaker. Allow to cool.

Remove the cooled crucible with platinum-tipped forceps and set on a clean tissue. Discard the water in the beaker and rinse the beaker. Wipe off the outside surface of the crucible and stand it in the beaker. Place a Teflon-covered micro magnetic stirring bar in the crucible and set on a magnetic stirrer.

Overflow the crucible with 60 ml HF (1:9), start stirrer and cover the beaker with a plastic watch glass. Stir until fusion is disintegrated.

Stop stirrer, tilt the beaker and lift the crucible with a plastic rod to check for completeness of disintegration of the fused mass. (Turbidity in the solution is mainly due to insoluble fluorides, not to undissolved fusion). If disintegration is complete, set the crucible upright in the beaker, leaving the former half full of the suspension. Overflow the crucible with 100 ml of the boric acid solution and stir again until clear.

Rinse off and remove the crucible, leaving the stirring bar in the beaker. Stir again for a minute or two, or until the solution is clear. Remove the bar with a magnet and transfer the solution to a 200-ml volumetric flask. Dilute to volume and transfer to a polyethylene bottle.

Label the bottle with sample number, actual weight of sample (w mg) and date. When analyzing an unknown, calculate true content for each element by multiplying observed values by 200/w. When using standard solutions prepared from international reference rocks, use the tabulated content (Table III) for each element, multiplied by w/200.

Pipette 50 ml of a sample solution into a 100-ml volumetric flask, add 20 ml strontium solution, dilute to volume and transfer to a polyethylene bottle. Label the bottle with the date and the sample number followed by "-50" - e.g. "AGV-1 - 50", indicating the presence of 50 mg of sample in 100 ml.

Similarly prepare a solution using 10 ml of sample solution and 10 ml strontium solution in a final volume of 100 ml. Label with date and sample number followed by "-10". If the sample is high in magnesium (see Table I) an additional solution may be required, containing 5 or 2 mg of sample, but the volume of strontium solution used should be 10 ml in each case.

Operating Parameters

Table I gives the appropriate settings to use for the determination of each element.

With the nitrous oxide-acetylene flame, the positioning of the burner to give maximum absorption is much more critical than with the air-acetylene flame. The use of the lens mask, with a 5-mm diameter opening, facilitates selection of the flame area for maximum absorption. It is important that the burner be carefully aligned before taking readings, particularly with the nitrous oxide flame.

While either the burner head with the 10-cm slot or the grooved head, with the 6-cm slot, may be used with the air-acetylene flame, only the latter may be used with the nitrous oxide-acetylene flame.

In using the air-acetylene flame, follow the instructions in Part 2, p. 17 (Abbey, 1968).

To use the nitrous oxide-acetylene flame, replace the burner head with the grooved head having the 6-cm slot. Ignite the flame with air and acetylene in the normal way. Check the pressure of the nitrous oxide supply, adjusting it if necessary to equal that of the air supply. Using the gas control unit, reduce the air pressure to 15 psi. Using a screwdriver, open the needle valve at the side of the gas control unit and simultaneously reduce the pressure of acetylene until a luminous flame is produced at an acetylene pressure of 2.5 psi. Without changing the needle valve, increase the acetylene pressure to 8 psi, and quickly change the "changeover" valve from "AIR" to " N_2O ". The resulting flame should have a red "feather" about 1 cm high. (If necessary, adjust the needle valve to attain this condition.) The acetylene supply must not be reduced to the point where the red feather disappears. In using this flame to determine a particular element, the acetylene pressure as well as the burner position must be adjusted to give a maximum absorption signal, but the acetylene supply should not be increased to the point where the flame is so luminous that there is excessive carbon build-up on the burner slot.

In prolonged use, the regulator on the nitrous oxide cylinder becomes cold, resulting in condensation on it of atmospheric moisture. In extreme cases, this condensate may freeze, thereby interfering with the operation. The difficulty may be overcome by applying gentle heat to the regulator, e.g. by means of heating tape, or with an ordinary incandescent bulb placed an inch or two from the regulator.

To extinguish the nitrous oxide flame, first change the changeover valve back to "AIR", and as soon as the flame becomes highly luminous, reduce acetylene pressure to 2.5 psi. Using a screwdriver on the needle valve, simultaneously reduce the acetylene flow and increase its pressure to

obtain a slightly luminous flame at 7.5 psi acetylene pressure. Increase the air pressure to 18 psi, and if necessary adjust the acetylene needle valve to restore the normal operating condition for the air-acetylene flame. Turn off the acetylene supply and allow the airflow to continue for a short time after the flame is extinguished to ensure that all acetylene is out of the system. Turn off the nitrous oxide supply, and then change the changeover valve to "N₂O" to drain that gas out of the lines. Change back to "AIR" and allow air to flow for a short interval to flush any residual nitrous oxide out of the system. Finally, turn off the air supply.

Analysis of Samples

For each component of each sample, obtain a first approximation of the concentration by rough comparison with any standard containing a comparable amount of the component in question.

For final analysis, compare each component of each sample with two standard solutions, one containing slightly more, the other slightly less of the component than expected in the sample. For most cases, the following sequence of readings should be used:

H - x - L - x - H - x - L

where H is the "high standard"

x is the unknown

L is the "low standard"

For silica and alumina determinations, readings are generally more erratic than for the other elements, so it may be necessary to extend the sequence to:

H - x - L - x - H - x - L - x - H - x - L

For most components, measurements may be made directly as absorbance, but for silica and alumina it is preferable to take readings as transmittance and to calculate absorbance. In all cases, the apparent content of the desired component is calculated separately for each "x" by interpolation between the immediately adjacent readings of "H" and "L". Wherever possible, "base-line" readings (with water aspirating) should be taken between all readings, and used as corrections, without adjusting instrumental settings. After values have been calculated for the three or five "x" readings, any obviously aberrant values are rejected, and mean values are calculated.

TABLE I
Operating Parameters

Component	Lamp Current mA	Range per cent	Sample mg/100 ml	Strontium ppm	Flame %	Slit microns	Wave Length A
SiO ₂	12	30-80	50	3000	N ₂ O-C ₂ H ₂	100	2516
Al ₂ O ₃	11	0.1-20	50	3000	N ₂ O-C ₂ H ₂	100	3093
Fe ₂ O ₃ T*	8	1-40	10	1500	Air-C ₂ H ₂	50	2483
MgO	4	0-15	10	1500	Air-C ₂ H ₂	100	2852
		5-30	5	1500	Air-C ₂ H ₂		
		20-50	2	1500	Air-C ₂ H ₂		
CaO	8	0-0.5	50	3000	N ₂ O-C ₂ H ₂	100	4227
		0.5-3.0	10	1500	N ₂ O-C ₂ H ₂		
		1-20	10	1500	Air-C ₂ H ₂		
Na ₂ O	5	0.1-10	10	1500	Air-C ₂ H ₂	50	5889
K ₂ O	5	0.1-1.0	50	3000	Air-C ₂ H ₂	300	7665
		1-10	10	1500	Air-C ₂ H ₂		

* Lens mask used with N₂O-C₂H₂ flame.

* Total iron, expressed as equivalent Fe₂O₃.

o In some cases, the burner must be rotated to attain the indicated concentration range.

TABLE II

Results Obtained on International Reference Samples
(all in per cent)

Sample	Method	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MgO	CaO	Na ₂ O	K ₂ O
GA	Acid	-	-	2.72	1.01	2.48	3.51	4.03
	LBF	69.66	14.80	2.81	1.02	2.50	3.51	4.03
	VR	69.90	14.50	2.86	0.95	2.45	3.55	4.03
GH	Acid	-	-	1.28	0.04	0.73	3.97	4.80
	LBF	75.52	12.62	1.35	0.04	0.68	3.86	4.75
	VR	75.80	12.50	1.33	0.03	0.65	3.80	4.78
BR	Acid	-	-	12.79	13.22	13.98	3.03	1.41
	LBF	38.72	10.30	12.90	13.38	14.16	3.00	1.39
	VR	38.20	10.20	12.92	13.28	13.74	3.05	1.40
G-2	Acid	-	-	2.77	0.78	2.02	4.01	4.48
	LBF	68.96	15.69	2.72	0.75	2.05	4.05	4.51
	PV	69.22	15.33	2.67	0.77	1.98	4.06	4.49
GSP-1	Acid	-	-	4.34	1.00	2.03	2.79	5.50
	LBF	67.68	15.02	4.23	1.01	2.06	2.78	5.46
	PV	67.27	15.18	4.26	0.98	2.06	2.77	5.50
AGV-1	Acid	-	-	6.90	1.50	4.97	4.26	2.89
	LBF	59.59	17.17	6.66	1.58	5.00	4.25	2.96
	PV	58.97	17.01	6.73	1.53	4.94	4.26	2.86
BCR-1	Acid	-	-	13.18	3.46	6.84	3.32	1.69
	LBF	54.22	13.48	13.40	3.48	6.96	3.36	1.76
	PV	54.36	13.56	13.40	3.46	6.94	3.26	1.67
PCC-1	Acid	-	-	8.19	43.46	0.64	0.02	0.00
	LBF	41.92	0.71	8.11	43.13	0.53	0.02	0.00
	PV	41.90	0.73	8.23	43.37	0.53	0.01	0.00
DTS-1	Acid	-	-	8.50	49.79	0.18	0.02	0.00
	LBF	40.17	0.28	8.60	49.56	0.16	0.02	0.00
	PV	40.66	0.29	8.59	49.75	0.14	0.01	0.00

NOTES

Acid - Acid decomposition (Abbey, 1968), other reference samples used as standards.

LBF - Proposed lithium fluoborate scheme.

VR - "Valeurs recommandés" (Govindaraju, pers. comm.)

PV - "Proposed values" (Abbey, in press).

Fe₂O₃T - Total iron, expressed as Fe₂O₃.



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TABLE III

Compositions of Standard Solutions
(per cent equivalents)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ T	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	BaO	SrO	Cr ₂ O ₃	NiO
GA	69.90	14.50	2.86	0.95	2.45	3.55	4.03	0.38	0.09	0.10	0.04	0.00	0.00
GH	75.80	12.50	1.33	0.03	0.65	3.80	4.78	0.09	0.05	0.00	0.00	0.00	0.00
BR	38.20	10.20	12.92	13.28	13.74	3.05	1.40	2.62	0.21	0.11	0.04	0.05	0.03
G-2	69.22	15.33	2.67	0.77	1.98	4.06	4.49	0.48	0.04	0.21	0.06	0.00	0.00
GSP-1	67.27	15.18	4.26	0.98	2.06	2.77	5.50	0.65	0.04	0.14	0.03	0.00	0.00
AGV-GSP	63.12	16.10	5.50	1.26	3.50	3.52	4.18	0.86	0.07	0.14	0.06	0.00	0.00
AGV-1	58.97	17.01	6.73	1.53	4.94	4.26	2.86	1.06	0.10	0.14	0.08	0.00	0.00
BCR-1	54.36	13.56	13.40	3.46	6.94	3.26	1.67	2.24	0.19	0.07	0.04	0.00	0.00
BCR-BR	46.28	11.88	13.16	8.37	10.34	3.16	1.54	2.43	0.20	0.09	0.04	0.02	0.02
BR-PCC	40.05	5.46	10.58	28.32	7.14	1.53	0.70	1.32	0.16	0.06	0.02	0.24	0.18
PCC-1	41.90	0.73	8.23	43.37	0.53	0.01	0.00	0.01	0.12	0.00	0.00	0.44	0.32
DTS-1	40.66	0.29	8.59	49.75	0.14	0.01	0.00	0.01	0.13	0.00	0.00	0.64	0.31