

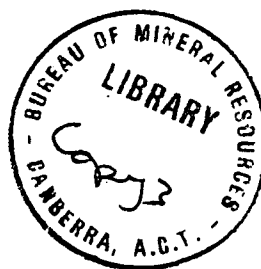
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COMMONWEALTH OF AUSTRALIA

DEPARTMENT OF NATIONAL DEVELOPMENT
BUREAU OF MINERAL RESOURCES
GEOLOGY AND GEOPHYSICS

RECORDS:

1965/54



REPORT ON MELBOURNE VISIT, FEBRUARY 17-19, 1965.

by

N.J. Marshall

The information contained in this report has been obtained by the Department of National Development, as part of the policy of the Commonwealth Government, to assist in the exploration and development of mineral resources. It may not be published in any form or used in a company prospectus without the permission in writing of the Director, Bureau of Mineral Resources, Geology and Geophysics.

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ABSTRACT

This record gives in detail the results of discussions held with experts on atomic absorption analysis, atomic absorption instrumentation, mineral analysis and flotation at various C.S.I.R.O. and University establishments in Melbourne during February 17th to February 19th, 1965.

Many specific and general problems were discussed in these fields.

Details of important new developments in atomic absorption and mineral analysis have been obtained in advance of publication, and it is recommended that suitable equipment be purchased to introduce these techniques as soon as possible.

A general outline of laboratory flotation cells, their cost, sources of supply and operation is given and it is pointed out that installation of a flotation cell could greatly improve the scope of mineral separation techniques for mineragraphic, geochemical and age determination investigations.

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During a recent visit to Melbourne to discuss latest developments in Atomic Absorption Spectrophotometry, discussions were held with the following people.

Dr. Walsh - C.S.I.R.O., Chemical Physics Laboratories, Fisherman's Bend.

The founder of atomic absorption methods of analysis in 1955. Designed the earliest instruments and the proto-types from which the Techtron AA3 was developed. Concerned principally with physical and electronic aspects and the development of improved spectral lamp sources and instrumentation principles.

Dr. Willis - C.S.I.R.O. Chemical Physics Laboratories, Fisherman's Bend.

Collaborator with Dr. Walsh but concerned with the chemical rather than physical aspects of atomic absorption research. Investigated analytical methods of atomic absorption for specific purposes (e.g. metallurgical control) and developed solvent extraction procedures for detection of low metal levels in pathological samples. Has done detailed work on chemical interference effects, development of hotter flames and improved burners.

Mr. Pilkington - C.S.I.R.O. Chemical Physics Laboratories, Fisherman's Bend.

Experienced analyst (Lemprier's, Sydney; C.S.I.R.O., Melbourne) with knowledge of many general and specific analytical techniques for analysis of metals and ores. Currently engaged in analysis of beach sands. Uses atomic absorption as an applied analytical tool and has investigated interferences in copper and chromium determination.

Mr. Trahar - C.S.I.R.O. Ore Dressing Laboratories, University of Melbourne.

Expert on flotation, particularly of non-sulphide minerals. Demonstrated flotation cells and provided much useful information on prices, types, sources, accessories, flotation chemicals etc.. Discussed the problem of flotation of micas from granites - a problem which has much bearing on geochemical exploration for tin and also age determination, as flotation provides a rapid method of fairly large scale mineral separation.

Mr. Drews - C.S.I.R.O. Ore Dressing Laboratories, University of Melbourne.

Analyst concerned with analytical control of processed ores and mill products. Provided useful references on selective mineral attack, although he has not used this approach himself.

Dr. McLaughlin - Geochemistry Department, University of Melbourne.

Discussed problems he and his research students have had with atomic absorption analysis with Dr. Willis and I. Research students were present during the discussion. Also discussed the flotation separation of biotites and passed on a useful scheme of rapid silicate analysis by chemical methods. This has been accepted for publication in *Analytica Chimica Acta*.

Mr. Biskupsky - Geochemistry Department, University of Melbourne.

Analyst on Dr. McLaughlin's staff. Gave details of a new method of rapid sample fusion to be published shortly in *Analytica Chimica Acta*. Also provided a text-book reference (in Russian) covering aspects of selective mineral attack for differential analysis of ores.

Mr. Mathews - Geochemistry Department, University of Melbourne.

Lecturer on Dr. McLaughlin's staff. Discussed geochemical work on tin content of muscovites from N.E. Victoria. Discussed his methods of sample digestion, sample preparation and analysis. Currently interested in the study of mercury dispersion, particularly at Captain's Flat N.S.W. - he proposes to use emission spectroscopy using "boiler" electrodes.

Mr. Amos - Techtron Pty Ltd., 271 Huntingdale Road, East Oakleigh, Victoria.

Note new address. Engaged in developmental work for Techtron Pty Ltd., manufacturers of atomic absorption apparatus. Demonstrated a stainless steel burner using acetylene/nitrous oxide to Dr. Willis and I at the C.S.I.R.O. Laboratories.

Drs. Walsh and Willis are also technical consultants on atomic absorption spectroscopy to Techtron Pty Ltd..

Dr. Willis gave up much of his valuable time in discussions over three days, and also arranged contact with Messrs. Pilkington, Trahar and McLaughlin, who in turn arranged contact with other members of their staff.

I would like to record the very generous co-operation of the people listed in giving much of their time and passing on information involving many man-hours of research.

Details of discussions held are given in the remainder of this report.

DISCUSSION WITH DR. WALSH

N.J.M. - "What is the reason for slight non-linearity of some graphs, particularly cobalt and nickel" ?

Walsh - "The main cause of non-linearity is the development of background emission of hydrogen continuum, the hydrogen being released by atomic bombardment of the glass walls of the lamp. This can be overcome by running the lamps overnight at reversed polarity and about 5ma current. Non-linearity of cobalt, in particular, and nickel (to a lesser extent) is also due to the presence of high intensity interfering lines nearby, due to the complex spectra of these elements.

New high-intensity lamps have been developed, more details of which will be released at the forthcoming Spectroscopy Conference in Perth. These lamps will cost about twice as much as the present ones (i.e. about £40) but will not be commercially available for about 6 months.

These new high intensity lamps use a primary cathode of the metal to be determined, together with a surrounding cluster of auxiliary electrodes. The primary cathode is therefore only heated gently by the passage of a small current, while the auxiliary electrodes carry a high voltage which excites the atoms released by the primary cathode.

These high intensity lamps do not excite interfering lines - therefore straight line plots are obtained for nickel and fairly straight ones for cobalt. High intensity lamps also, by their design, have a more stable output, permitting more accurate readings and greater scope for scale expansion (i.e. less noise).

- N.J.M. - "Do lamps deteriorate on storage " ?
- Walsh - "No. On prolonged storage lamps do develop a hydrogen continuum and it would be advisable to give them a burst of reverse polarity current every 6 months".
- N.J.M. - "With some elements, such as Zn, sensitivity is so high that it can actually be an embarrassment in geochemical work. I have reduced sensitivity for Zn by restricting the burner slit and reducing the air pressure - thereby achieving a sensitivity reduction of about seven-fold.
- Walsh - "This is quite good. A more drastic sensitivity reduction, of about twenty-fold, can be achieved by rotating the burner through 90° .
- N.J.M. - "Butler has proposed a burner using a series of flames at 90° to the light path. By using such a "wide flame", the effective aperture of the diffraction grating should be filled and therefore the instrument may be more efficient. Would you agree" ?
- Walsh - "The fact that the instrument works at full efficiency is proved by the fact that your calibration graphs are straight lines in most cases and that a strong standard solution gives full scale deflection."
- N.J.M. - "What about multi-hole burners",?
- Walsh - "These are not advised - the holes are difficult to keep clean, and the flame is often unstable. Multi-hole burners were used with gases such as oxy-acetylene where flame velocity is very high and it is difficult to pre-mix the gases. High velocity flames, such as oxy-acetylene, oxy-hydrogen and oxy-cyanogen (toxic!) are difficult to control and there is always the danger of explosion".
- N.J.M. - "What about water-cooled burners"?
- Walsh - "These are not recommended - the cooling causes condensation of the aerosol which can block the burner slit. There is no real gain in sensitivity by using water cooled burners.
- N.J.M. - "Is it true that an Eel type atomizer is the most efficient and has the lowest consumption rate".
- Walsh - "The Eel type atomizer is generally the most efficient, but consumption and efficiency depends on adjustment of the capillary. This is very critical, and consumption vs. atomizer efficiency curve rises steeply at first, then flattens off at about 4 to 5 ml per minute consumption. Above this rate efficiency does not increase much. The Techtron atomizer is a copy of the Eel type.
- N.J.M. - "Yes, this is what I found - that atomizer consumption could be reduced from 10 ml to 5 ml by changing the length and diameter of the outside aspirator tube.
- Walsh - "Yes, the same effect is simulated by moving the atomizer capillary forward a few thousandths of an inch at a time - both methods control pressure gradient. ~~He demonstrated~~ an adjustable atomizer made by C.S.I.R.O."
- N.J.M. - "What about ultra-sonic atomization?

- Walsh - "This has been tried but found to be rather complex and time consuming. It is not a great improvement, as sensitivity only rises two or three-fold. It is felt that this approach does not have much merit.
- N.J.M. - "What about arc vaporization of solid samples",
- Walsh - "The difficulty here is in obtaining a constant vaporization rate for the sample - matrix effects become critical and many of the advantages of atomic absorption over emission are lost. Cathodic sputtering has been used with success on metals and alloys - this method being confined to conducting samples. Laser excitation only lasts for a few micro-seconds and therefore does not have enough duration. The L'vov furnace is too complex in design and operation. A disadvantage of the L'vov furnace is that the photo-multiplier is over-worked through being exposed to such an intense white light emitted by black body radiation (white hot graphite).
- N.J.M. - "Lamps such as arsenic giving very weak emission require extreme amplification to give full scale readings, with consequent high noise levels. Have there been any improvements in arsenic line sources"?
- Walsh - "Mr. C.S. Rann of A.N.U. has pursued radio frequency excitation but not with complete success. We feel that the new high intensity lamps being developed will be satisfactory for arsenic, too, although initially commercial production will be limited to the more commonly used lamps."
- N.J.M. - "What advantages, if any, are there in electronic modulation over mechanical modulation using a rotating sector disc.?"
- Walsh - "There is no difference in the end result, except that it is technically easier to construct a receiver tuned to an electronic modulator source".
- N.J.M. - "Are there any other atomic absorption units, possibly of a more sophisticated nature, which you would recommend?"
- Walsh - "The Techtron AA-3 is as good as any, and has a superior monochromator to most. The Perkin-Elmer is probably the only other comparable instrument, at about three times the price. At the Pittsburg conference early in March, Techtron will announce a new model atomic absorption instrument using a lamp source as resonance radiation receiver in lieu of a monochromator. This arrangement is simpler but not as versatile as your AA-3 instrument. However by means of this arrangement the cost of the monochromator, a major item, is obviated. This instrument is intended only as a simple cheap instrument to run on a fixed program - it will not be as versatile as the AA-3 model. The principle of this instrument can be used to develop a multi-element direct reader atomic absorption unit; further details will be announced at the Perth conference during May 31st - June 2nd.

DISCUSSION WITH DR. WILLIS

- N.J.M. - "What progress has been made in the field of flame types, and what are the advantages of air/acetylene, oxy/hydrogen, air/coal gas and air/propane flames"
- Willis - "Air/coal gas and air/propane are low temperature flames which in general are not as useful as air/acetylene, the best "all-round" flame. Moreover, low temperature flames are subject to more chemical interference in the flame, (e.g. sulphate or phosphate suppresses sensitivity) than high temperature flames.

Oxy/hydrogen mixtures give very hot flames but because of the very high flame velocity, it is difficult to pre-mix the gases and introduce the aerosol into the flame. Moreover there is a constant danger of explosion with oxy/hydrogen burners, due to this high flame velocity. The same situation also applies to oxy/acetylene - i.e. a hot flame but a rather high flame velocity.

Amos has proposed a gas mixture of acetylene and nitrogen/oxygen (a 50:50 mixture). This produces a very hot flame, almost as hot as oxy-acetylene without the disadvantages of high flame velocity. However a slight danger of explosion still exists, the flame velocity being between that of air/acetylene and oxy/acetylene. There is also the problem of obtaining supplies of nitrogen/oxygen mixture, which has to be made to order by C.I.G.

A recent innovation is to burn acetylene with nitrous oxide. The latter is available ready-made as an anaesthetic and is not expensive. The flame velocity is almost the same as with air/acetylene flames, yet a very hot flame (temp. $2,950^{\circ}\text{C}$) results.

This hot flame is useful in reducing chemical interference effects, and analysis of refractory elements by atomic absorption is now possible for the first time.

For instance, 1 part per million of aluminium can now be detected in solution, whereas before the detection limit was in excess of 1,000 ppm (air-acetylene flame). Similarly, 100ppm vanadium gave 12% absorption, compared to 1% absorption for at least 1,000 ppm V previously.

Beryllium can now be detected to .02 ppm (2 ppm Be give 37% absorption) (previous detection limit 100 ppm). Boron can now be detected to 100ppm.

[By analogy, similar spectacular improvements should result in detection limits for Mo, Ba, Nb, W, when using a hot acetylene/nitrous oxide flame.]

[A demonstration was given of the acetylene/nitrogen-oxygen and acetylene/nitrous oxide flames using 2" and 4" burners and 100 ppm Al as standard. Burner temperature was monitored with a thermocouple, and rose slowly to about 180°C after 15 minutes. The sensitivity was seen to be slightly dependant on burner temperature - Dr. Willis is investigating this aspect further.]

[To light the acetylene/nitrous oxide flame, the acetylene supply is turned on first and ignited - an exhaust fan is necessary to remove soot from the flame.

The nitrous oxide supply is then turned on, the reverse procedure being used for turning off. The flame is quite docile and safe to use.]

N.J.M. - "What types of burners are used"?

Willis - "The tubular type of burner at present in use cannot be used with such hot flames, which induce sagging of the burner and opening up of the slit. A new type of burner has been developed for all gas mixtures, which consists of two machined steel plates about a quarter of an inch thick, which are clamped edge to edge, the slit width being determined by the thickness of metal inserts at each end. These burners are secured to a glass spray chamber, the latter having a tapered ground glass joint which slips into the Techtron burner body. Burners are thus interchangeable, and the thick steel prevents blow-back of the flame.

A 10 cm burner with a .018" slit based on this construction is proposed for the new air/acetylene burner to be manufactured shortly by Techtron.

This burner can also be used for acetylene with nitrogen/oxygen or nitrous oxide, or with air/hydrogen.

However there is some "feathering" (with consequent instability) of the 4" narrow slit flame when used with acetylene and nitrous oxide, and it has been found better to use a short, fat flame rather than a long narrow one which suffers more cooling by the atmosphere for this gas mixture. Thus a 2" x .025" burner is proposed for acetylene/nitrous oxide, and gives superior sensitivity to the 4" (10cm) burner.

Even greater sensitivity with air/hydrogen reducing flames can be achieved by using a wide flame provided by a 10 cm x .035" burner instead of the normal (10 cm x .018") burner used for air/acetylene. However when using wide slot burners with air/hydrogen, a perspex screen must be used in case of explosion, and an auxiliary air inlet attached to the burner mixing chamber. This auxiliary air is fed into the spray chamber at a rate equal to that normally used (i.e. 6 litres/minute), then the normal air supply is turned on (combined air flow now 12 l/min), then the hydrogen is turned on and the flame ignited. The auxiliary air supply is then turned off, once the flame has been lit. The reverse procedure is followed for turning off the flame. If these precautions are not taken with the wide burner, an explosion will result.

For this reason, commercially available (Techtron Pty. Ltd.) burners for air/hydrogen will be the same as for air/acetylene, using a narrow slit. These do not require auxiliary air but are not as sensitive in operation as the wide slit burner.

[This is important in tin analysis].

N.J.M. - "Have you worked out specific methods for As, Se, Sn, Te, Sb, or Au which would be suitable for routine atomic absorption work on geochemical samples"?

Willis - "No, these elements have not been investigated thoroughly. Arsenic and tin are best determined in a wide air/hydrogen (strongly reducing) flame using auxiliary air, as described above.

With the air/hydrogen flame, scattering of short wavelength light (e.g. As 1937 Å, As 1971 Å) is considerably less than with air/acetylene reducing flames. Moreover the hydrogen flame is strongly reducing and therefore minimizes formation of refractory oxide molecules in the flame.

Maximum transmission of light is obtained with the light beam focussed through the dark tunnel of the flame. The interference from coloured fringes of the flame can be suppressed by confining the light beam to this central tunnel by means of a diaphragm of about $\frac{1}{4}$ " aperture placed over the front lens.

Under similar conditions, Amos obtained 0.65 transmission at 1972 Å for a 100 ppm As standard, and 0.57 transmission for the same standard at 1937 Å.

Tin is also best determined with the air/hydrogen flame.

Tin sensitivity has been investigated by both Amos and Allen, who found that to obtain 90% transmission, 128 ppm Sn was required with an oxygen-enriched air/acetylene flame, 35 ppm Sn was required for an air/acetylene flame and only 4.4 ppm Sn for an air/hydrogen flame.

[- Thus the sensitivity at 2246 Å for an air/hydrogen wide flame is adequate for geochemical investigation of tin -].

N.J.M. - "We have experienced non-atomic absorption due to the presence of mixed salts of Fe, Na, K, Mg, Ca, Al etc. when geochemical samples are aspirated into the flame. This has been negligible at the higher wavelengths, (e.g. Cu 3247 Å) but is appreciable at short wavelengths - e.g. Zn 2137 Å, Te 2142 Å, As 1937 Å. What can be done to overcome this?"

Willis - "This effect is actually an apparent absorption caused by loss of light through scattering by solid particles in the flame. It is more serious at the shorter wavelengths you mention, and is also more serious with the alkaline earths than the alkali metals. It is described on page 72 of my paper "The determination of copper in butter and butteroil by atomic absorption spectroscopy" (Aust. Journ. Dairy Technology - June 1964, p.70-74).

Nothing can be done to physically overcome this. It can be corrected by choosing a suitable non-absorbing line near to the resonance line - e.g. 3338 Å for copper, measuring the scattering at this line and subtracting this value from the measured absorption at the resonance line. The problem is to find a line sufficiently close which does not absorb."

N.J.M. - "This technique could be applied in the case of zinc 2138 Å resonance line, where scattering can be serious, by measuring the scattering using the tellurium lamp and the 2142 Å line - always assuming, of course, that no detectable tellurium occurs in the sample."

Another method of course is solvent extraction of the element being sought, say zinc in the presence of mixed salts. This is normally rather time consuming, and I wonder if one could instead take aliquots of each sample solution in a batch, lump the lot together, remove zinc by solvent extraction and then use this aggregate sample solution, minus the zinc, as an average blank. This could be sprayed into the flame instead of distilled water, with the instrument set to zero - then the 'true' absorption due to zinc in each sample solution can be determined by the usual method - relating absorption to the blank instead of to the distilled water. This method pre-supposes that geochemical sample solutions are of sufficiently similar composition, and that the scattering effect due to mixed salts is not critically dependant on salt concentration, so that the principle of using an "average blank" is valid.

One could use the same approach by monitoring scattering using a tellurium 2142 Å line."

Willis - "This seems a feasible method, provided you have tested the variation of scattering on a batch of test samples, and established this scattering to be more or less constant."

N.J.M. - "I have investigated solvent extraction procedures and found that butyl alcohol, amyl alcohol, amyl acetate and acetyl acetone are the only solvents which can be sprayed into the flame without altering its characteristics. Other solvents either extinguish the flame, or, in the case of methyl isobutyl ketone which you use, give a smoky, luminous flame. I could not obtain methyl-n-amyl ketone, also used by you. "

Willis - "Oxygen-containing solvents are necessary. However the solvents which you found give smoky flames can be used if the amount of solution entering the atomizer is restricted. In this case, even kerosene, para-xylene and the ketones can be used. Presumably, if the amount of solvent entering the flame is restricted, then the sensitivity must also be restricted. Therefore for any one combination of conditions the freely aspirating solvents such as butanol would still be more effective 7.

Methyl-n-amyl ketone was used as this had a slightly lower solubility in water than methyl isobutyl ketone.

One method of restricting atomizer uptake is by restricting the capillary tube aspirator, e.g. use intramedic polythene tubing, No.50 (I.D. .023" x O.D. .038") into which is fitted intramedic No.10 tubing (I.D. .011" x O.D. .024"), with the joint sealed by duco cement."

N.J.M. - "You have used ammonium pyrrolidine dithiocarbamate for solvent extraction of heavy metals - e.g. Pb in urine. I have been investigating solvent extraction systems with sodium diethyldithiocarbamate. What advantages had the pyrrolidine complex?"

Willis - "It was felt that ammonium salts are preferable to sodium salts because of possible sodium interference in the flame. The pyrrolidine compound is more specific than diethyldithiocarbamate and can be used in an acid solution. This was convenient for work on urine, which is normally preserved in acetic acid and which gives troublesome precipitates in alkaline solution. "

N.J.M. - "I found that iron consumes the reagent in acid solution and to effectively suppress iron interference, an alkaline citrate medium must be used - hence I abandoned this reagent in preference to diethyldithiocarbamate. "

Willis - "I had no occasion to investigate iron interference, as iron is only present in low levels in urine. In your geochemical samples, it is an important factor, of course. "

N.J.M. - "Have you a summary of Malissa and Schoffman's paper (in German) which appeared in Mikrochimica Acta 1955, p.187"?

Willis - "Yes - two mistakes appear in the original paper, however. The melting point of the pure ammonium pyrrolidine dithiocarbamate is 138°C, not 128°C, and their figures for S and N analysis should be interchanged. The purity of the product is fairly critical for this work.

Ammonium pyrrolidine dithiocarbamate will form precipitates with the following metals in the pH range 2-14.

Ag, Au, Bi, Cd, Co, Cu, Fe²⁺, Fe³⁺, Hg, Mn, Ir, Ni, Os, Pb, Pt, Pd, Rh, Ru, Tl, Zn.

At pH 2-6, the following metals precipitate

As³⁺, Cr, Mo, Te, V.

At pH 2-4

Nb, U

At pH 2-8

Sn^{2+}

At pH 2-9

Sb^{3+} , Se

At pH 2

W - Amos has detected tungsten to 20 ppm by atomic absorption.

N.J.M. - "When using your ammonium pyrrolidine method for lead extraction, I found that the organic phase became saturated at low concentration levels, about 20 ppm - above this concentration an insoluble scum formed at the reagent interface. Using sodium diethyldithiocarbamate this did not occur."

Willis - "I was not aware of this.
 / We subsequently carried out tests in the laboratory and found that better results were obtained if the solvent was added first, then the complex added and the solution shaken immediately rather than the reverse procedure. At higher concentrations, however, the metal complex formed an insoluble scum at the solvent interface. This did not occur with Willis' work with pathological samples low in metal content, but can be serious with geochemical samples, where Willis suggested the diethyldithiocarbamate approach may be better.

Three references were recommended by Willis.

1. Economic Geology vol. 59, page 240-258
2. Methods of Biochemical Analysis, vol XI, Interscience Publisher - includes several chapters on atomic absorption analysis by Willis.
3. Nature, vol. 199, no. 4893, p.552-3 - for Au and Ag analysis. "

DISCUSSION WITH MR. PILKINGTON

Mr. Pilkington has used atomic absorption for routine analysis of beach sand materials. He stressed the importance of using standards which approximate as closely as possible, with respect to both anion and cation, to the bulk composition of sample solutions. His figures below illustrate the effect of foreign ions on 10 ppm copper response with atomic absorption.

<u>Standards</u>	<u>Absorption</u>	<u>Standards</u>	<u>Absorption</u>
10 ppm Cu alone	.660	As at left, but with	-
" " " + 1N HCl	.625	1% Fe also present.	
" " " + 1N HNO ₃	.605		.535
" " " + 3.6N H ₂ SO ₄	.505		.555
" " " + 4N H ₃ PO ₄	.470		.425
" " " " 2N H ₃ PO ₄ + H ₂ SO ₄	.485		.415
			.460

He prefers an acid pyrosulphate fusion for sample attack of materials such as beach sands.

He suggested that an $\text{HF}/\text{H}_2\text{SO}_4$ digestion would be suitable for solution of Ti and Sn bearing samples, and in this "non-aqueous" system, volatile Ti and Sn fluorides would not be lost provided sulphuric acid was present to convert these to sulphates - the HF being necessary to destroy silicates and remove silica.

He agreed that with HF alone, tin might be lost as the volatile tetrafluoride on evaporation to dryness.

He had not worked with perchloric acid digestions, since other methods are equally suitable and the use of perchloric acid on a routine scale may be dangerous.

He suggested that Groves' book on silicate analysis might indicate methods of approach for differential mineral attack, but had not done any work on this himself.

DISCUSSION WITH MR. TRAHAR

N.J.M. - "What types of flotation cells are available for laboratory work involving mineral separations of samples up to say 1 kg. capacity."

Trahar - "The 500 gm. capacity cell is the best for your purpose. The best types are:

1. Denver - supplied through A.E. Goodwin, Sydney.
The model D-1 unit costs £510, and can be supplied with 250 gm, 500 gm. and 1,000 gm. glass or stainless steel cells at about £30 each for glass cells and £25 each for stainless steel. Thus one can do an initial float with the 1000 gm. cell and finish up with the 250 gm. cleaner cell float. The unit is supplied with an attritioning attachment (= "conditioning" attachment) which breaks up and stirs the particles with the air turned off, and an agitating attachment. A tachometer can be fitted for an extra £50 but is not necessary.
2. Wemco - Fagergren, supplied through Warman, Sydney.
This costs £370 supplied with attrition and agitation attachments and a glass 600 gm. cell. A stainless steel 2,000 gm. cell is also available for about £30. A tachometer is not offered.
3. Wedag, supplied through Wollongong Engineering, Wollongong.
Costs £217 supplied with 1, 2, 3, 4, 5, 6 litre capacity fleiglass cells but has no attritioning or conditioning attachment.
4. Booth - supplied from 333 West 14th South Street, Salt Lake City, Utah, U.S.A.
Cost £269 but is not very versatile, and there are no Australian agents.
5. Agitair - supplied by Edward Ling Co., 44 Grenfell Street, Adelaide.
This costs £414 supplied with three cells - 500g., 1000g., and 2,000 g. - made of clear plastic, has a swivel head, tachometer and overflow launder device to control agitation. However a pressure air supply is needed, whereas other machines pump their own air.

Of these cells, the Denver and the Wemco-Fagergren would be the best from the aspect of versatility in a research laboratory. "

N.J.M. - "Who are the agents for flotation chemicals "?

Trahar - "Cyanamid, Union Carbide Aust., and Chemical Materials Ltd. (Sydney) are the main ones for amines and fatty acids. Others are H.H. York (Melbourne) and Swift & Co., Melbourne - the Dow (U.S.A.) agents."

N.J.M. - "What load of solids, and what pulp concentration, is usually used"?

Trahar - "The cell capacity refers to the load of solid sample added. I usually use a 560g. sample for the 600 g. Fagergren cell. The cell is then almost topped up with water, about 20 to 25% of solids being present in the cell, and 75-80% water."

N.J.M. - "What reagent concentrations are used"?

Trahar - "In flotation practice, reagent concentrations are expressed as pounds per ton of dry solid (ore). 1 lb/ton is equivalent to $\frac{1}{4}$ gm. per 560 gm. of solid. (for the Fagergren 600 g. cell). Thus, if a 2.5% solution of reagent is prepared, then 1 ml. is equivalent to 0.1 lb./ton on a 560 g. sample. Reagents are usually added in concentrations of .02 up to 0.1 lb/ton.

Frother additions are less than collector additions, and usually not more than .05 lb/ton of Aerofroth 65 (from Cyanamid) or Dow Froth (from Swift) is used. These two frothers are the most commonly used for routine work. Amine reagents such as "Armeen 12" are commonly used as collectors, as well as xanthates."

N.J.M. - "By what means can selectivity control be achieved "?

Trahar - "There are three ways of obtaining selective flotation, provided the material is first deslimed to minus 5 or 10 microns. This is imperative as amines do not respond to slime (-10 micron) material."

1. pH control. This is important and a pH meter to monitor the cell is essential.

2. Collector addition (xanthate, amine, etc.).

3. Modifiers or depressants - e.g. addition of sodium silicate prevents quartz from floating.

N.J.M. - "What sort of separations, and to what limits, can be achieved by flotation"?

Trahar - "Many systems can be upgraded or concentrated. In the laboratory where time is available to re-float many times over, and economic aspects are not important, fairly pure concentrates can be obtained, whereas in the mining industry the concentrate grade obtained is of course a compromise between economics and grade.

Separations such as copper minerals from sphalerite and pyrite, galena from sphalerite and pyrite, and sphalerite from pyrite are well documented in the standard texts. 0.3% pyrite can be upgraded by several floats provided there is no carbonaceous matter.

Separations are largely a matter of art and experience, with a good deal of trial and error.

N.J.M. - "You stress the importance of desliming. How is this carried out"?

Trahar - "The crushed material is simply agitated in a bucket of water, then allowed to settle. Stokes Law is applied to calculate the depth of minus 10 micron slimes and after the nominated time interval, a siphon tube is lowered into the bucket and the slimes siphoned off. The tube is bent with a hole in the upper surface to maintain the critical depth and obviate loss of heavier particles.

The desliming process is repeated once more and then the plus 10 micron fraction is placed in the flotation cell."

N.J.M. - "Could you give a recipe for separation of mica from granites. This method would be a very rapid one by flotation, whereas the method we use, involving magnetic separation on a Frantz separator and heavy liquid work is very tedious, since many small sample aliquots have to be treated to give a large, representative sample.

The flotation approach therefore has real promise for mica separation for geochemical work (e.g. tin content) or age determination work."

Trahar - "Mica flotation from granites is very simple and rapid.

1. grind the sample to about minus 65 mesh.
2. deslime twice.
3. add solid to float cell, and make up to volume with water.
4. add sulphuric acid to adjust to pH 3.
5. add .05 lb/ton of "armeen 12" (an amine reagent), and .02 to .03 lb/ton of "aerofroth".
6. Condition (i.e. agitate in float cell) for 1 minute.
7. turn on air supply - mica will appear in the surface froth within 2 minutes.
8. when no more appears, add half quantities of collector and frother and repeat flotation.

This should give a fairly clean separation of biotite and muscovite from quartz and feldspar. Hornblende may accompany the concentrate, in which case further separation may have to be done, using a cleaner float (experiment to find best conditions) or heavy liquids, or a Frantz isodynamic separator. In any case, a rough concentrate can be obtained very quickly from a large sample."

N.J.M. - "How does one remove organic reagents"?

Trahar - "Normally the float concentrate is scraped off or allowed to overflow, then dried in a large oven using a fan to circulate air. If desired, the organic reagents can be removed by using suitable solvents such as Acetone.

N.J.M. - "What heavy liquids do you recommend besides the commonly used methylene iodide type"?

Trahar - "R.P. Cargill Laboratories, 117 Liberty Street, NY6, New York, U.S.A. are agents for an extensive variety of heavy liquids.

Thallium malonate formate mixtures give an S.G. range of 2.50 - 4.05, at a cost of about \$105 a pint. Generally it is best to avoid the malonates, however.

Mercury suspensions are available in a range of S.G. from 3.6 - 7.5, costing from 2.5 to 6.5 \$ per 15 ml.

A good reference on "Properties of heavy liquids" appears in the S.M.E. transactions for June 1963."

N.J.M. - "What standard texts on flotation can you recommend?"

Trahar - " 1. "Principles of Flotation", by Sutherland and Wark - available from the A.I.M.M. for £3.

2. "Flotation" by A.M. Gaudin, McGraw Hill, 1957 - cost £7. "

N.J.M. - "Have you any other comments to make?"

Trahar - "Yes - one very important aspect is the question of grinding; I mean grinding, not pulverizing of samples. Machinery such as the Pica Mill, Braun pulverizer and the Siebtechnik are all pulverizers of various capacities. These rapidly break down a sample for chemical analysis but produce a wide size spectrum of grain size, from fairly coarse particles to extremely fine ones. A disproportionately high percentage of slimes is produced by pulverizing.

We grind our samples by wet-grinding in a small ball mill - the process is slow and may take some hours, but is the only way in which a fairly uniform grain size suitable for clean flotation separation, is produced. Even then, desliming is necessary." [A suitable ball mill was demonstrated]

DISCUSSION WITH MR. DREWS

No specific problems were covered, but Mr. Drews kindly supplied references he had abstracted on selective mineral attack, mainly for systems such as native and oxide copper in minerals, selective dissolution of limonite in the presence of hematite, determination of chalcopyrite copper and bornite copper in ores, and selective dissolution of magnetite in the presence of ilmenite. Many of these references are in Russian.

DISCUSSION WITH DR. McLAUGHLIN, DR. WILLIS, AND RESEARCH STUDENTS, MELBOURNE UNIVERSITY.

A discussion was arranged during which problems encountered by research students using atomic absorption analysis were discussed. These were generally of a well-known nature and are covered elsewhere in this and other reports.

One student pointed out that anomalously high values were obtained for gold, which I suggested were due to interference by iron. He also noted a slight "enhancement" of cobalt sensitivity by sulphate, to the extent that in a 0.1% sulphate solution, with a trace of cobalt, 97.5% transmission was obtained instead of 99% transmission. It is felt that this effect is similar to that noted by Pilkington for copper, and is not really an enhancement, but an interference.

In this connection, Dr. Willis mentioned that with the hot acetylene/nitrous oxide flame, both fluorine and iron were found to increase Ti sensitivity.

The use of a $\frac{1}{4}$ " aperture disc placed over the front lens is recommended for chromium analyses, to confine the light beam to the central area of the flame, where the atom population is greatest. Dr. Willis mentioned that Pilkington found the valence state is important in chromium sensitivity, and he suspects pH may also have an effect on the working curves.

DISCUSSION WITH DR. McLAUGHLIN AND MR. BISKUPSKY

Routine silicate analysis and geochemical work has shown that residues frequently remain after the classical methods of attack. These residues are sometimes ignored but they can harbour large amounts of trace elements.

Many samples of graptolitic shales from Victorian goldfields yielded abundant residues of black, graphitic material after hydrofluoric acid digestion.

In a recent paper in *Geochimica et Cosmochimica Acta* the problem of residues after hydrofluoric acid attack in silicate analysis was discussed, and the following minerals identified in the residues of many samples: sillimanite, zircon, kyanite, andalusite, corundum, rutile, graphite, pyrite, chromite and barium sulphate.

The geochemistry department of Melbourne University investigated many alternative methods of sample attack, and finally came up with the boric acid/lithium fluoride fusion described below. This was developed by Mr. Biskupsky and has been accepted for publication in *Analytica Chimica Acta*.

Method

1. Prepare a fusion mixture in the ratio 1:3 of boric acid and lithium fluoride.
2. To 0.5 g powdered rock sample, add 4g. of fusion mixture, in a platinum crucible.
3. Heat at 900°C for 10 minutes.
4. Quench quickly in water and add 10 ml. conc. sulphuric acid.
5. Evaporate for 30 minutes under fume hood to remove volatile baron fluorides and silica as silicon tetrafluoride.
6. Dilute with water to volume and proceed with analysis.

This method, which was originally developed for silicate analysis, has immediate application to total trace element analysis. Thus a method of complete solution of silicates and resistant minerals is available to determine their trace constituents by chemical methods such as atomic absorption.

It has been tested extensively and found to be rapid and completely successful in all cases in taking the complete sample into solution. Even the resistant refractory minerals mentioned above are completely dissolved.

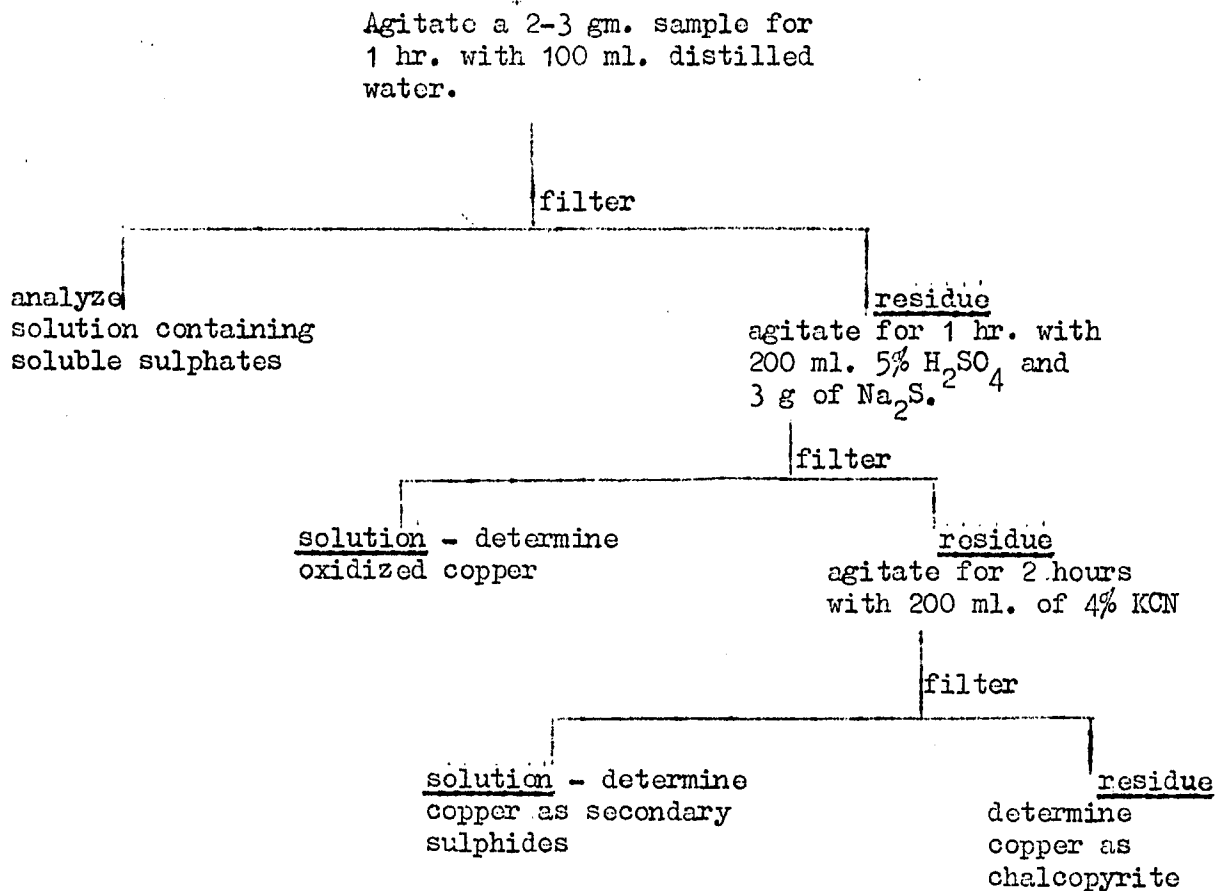
A method of rapid silicate analysis has also been published in the latest issue of *Analytica Chimica Acta*. This involves peroxide fusion of the sample in a nickel crucible, determination of silica by titration and of other elements by titration and colorimetry. A reprint of this was obtained. The authors' claim this to be the only published major advance in silicate analysis since the method of Shapiro and Brannock.

Mr. Biskupsky also had a useful reference book in Russian which discussed in detail some schemes for "phase analysis" of mineral components of ores. The analysis of various iron, copper, zinc and nickel ores was discussed.

The translated extract illustrates how the various components of a typical ore - water-soluble salts, oxidized copper, secondary sulphides and chalcopyrite can be chemically analyzed on the one sample.

A shaking machine is required for sample agitation.

Analysis of Copper Ore Phases



The translated Russian title of the book is "Technical Analysis of Ores of Coloured Metals" by S.A. Fionberg, Scientific Technical Edition, Moscow 1946.

If this book is out of print and not available through libraries, Mr. Biskupsky has agreed to lend it for photo-stating.

DISCUSSION WITH MR. MATHEWS

Mr. Mathews, a lecturer and research student in the department has examined the tin content of muscovite from pegmatites of a tin mineralized area in N.E. Victoria. He obtained erratic but high tin contents, up to 1,000 ppm in the muscovites (biotite was absent), but the area investigated was only a few miles wide and too small to outline a geochemical province relative to surrounding "background" rocks.

Pegmatitic muscovite was separated by hand picking, and determined chemically as well as spectrographically.

Chemical determination was by polarography after solution of mica by HF/H₂SO₄. Loss of tin did not occur by this method. Cassiterite, however, is not attacked by this method, which can in fact be used to separate intergranular cassiterite from muscovite.

Cassiterite was taken into solution by a complex method involving a double roasting ("calcining") in a current of hydrogen to reduce SnO₂ to metallic tin which was then dissolved in HCl.

Spectrographic determination was done by arcing the finely "chopped" mica with 50% Na₂CO₃.

The micas were finely chopped for these determinations by using a blast of air carrying the mica flakes to impel on a series of blades revolving at high speed. An instrument is available commercially and Mr. Mathews can supply further details of this or blueprints of a version he built himself.

He is currently interested in mercury dispersion, particularly at Captain's Flat, and hopes to be able to detect .01 parts per million of mercury using an 8 gm. sample, boiler electrode heated by a small electric furnace, and a Hilger Large Quartz spectrograph.

He would be very interested in establishing contact with anyone working in the field of mercury detection and mercury geochemistry.

DISCUSSION WITH MR. AMOS

Mr. Amos recently resigned from Sulphide Corp. and has joined the staff of Techtron Pty. Ltd., of 271 Huntingdale Road, East Oakleigh, Victoria on research and development in atomic absorption spectroscopy.

He has collaborated with Drs. Walsh and Willis in the development of new burners and hotter flames. This topic was adequately covered by both Walsh and Willis and no further information could be obtained.

Techtron expect to commence production of the new burners in about 6-8 weeks; as yet costs have not been worked out but they anticipate about £20 for the burner. Production of the new high intensity lamps is about 6 months away.

CONCLUSIONS

From the wealth of information on both general and specific problems, the following points are considered most important.

1. New high intensity spectral lamps have been developed. These are of high stability, promising more precise work through greater success with scale expansion.
2. New burners have been designed which are multi-purpose, require no maintainance, and are more robust for high-temperature flames than the present tubular design.
3. An important development is the use of the high temperature, low flame velocity nitrous oxide/acetylene flame. Use of this hot flame enables refractory elements such as aluminium, vanadium and titanium, to be determined by atomic absorption analysis for the first time. The hotter flame also suppresses chemical interferences in the flame and promises improvement in sensitivity for many "borderline" elements previously determined by air/acetylene flames.
4. A list of important references and a text dealing with atomic absorption analysis has been recommended.
5. A review of flotation cells, their features, cost and sources of supply is given. Instruction was given in the elementary aspects of flotation, including a "recipe" for flotation of micas from granites. Information was also obtained on heavy liquid media and several references on the subject of flotation are given.

6. New methods of rapid silicate analysis and total sample fusion were released by the University of Melbourne geochemistry department in advance of publication.
7. The importance of chemical interference in some atomic absorption analyses, and the need for careful investigation of these effects was stressed.

RECOMMENDATIONS

It is recommended that supplies of hydrogen and nitrous oxide gas be ordered as soon as possible to enable hot flame and strongly reducing flame techniques to be used.

Three new burners, one for air/acetylene, one for acetylene/nitrous oxide and one custom-built wide slit burner with tapping for auxiliary air supply for the air/hydrogen flame should be ordered as soon as prices have been decided on by Techtron Pty. Ltd.

Several high-intensity lamps should be ordered when these become available. They will be especially important for the elements Zn, Co, Pb, As, Se, Te, due to the low emission and inherent instability of the normal lamps.

The whole aspect of mineral separation should be reviewed and it is recommended that a flotation cell either of the Denver or Fagergren type be purchased together with accessories and a broad range of flotation reagents. Flotation can provide the means of rapid mineral separation for fairly large samples. Thus the routine work of biotite separation for age determination or selective geochemical analysis can be greatly simplified. Several staff members have indicated interest in a flotation cell, particularly Mr. I. R. Pontifex who feels that flotation of ores and beach sands would be a valuable technique to aid his mineragraphic investigations.

A 1 or 2 kg. capacity ball mill as well as a smaller capacity ball mill would be necessary if much routine flotation work is to be done. Wet grinding of samples in a ball mill is the only way to achieve a fairly uniform grain size with a minimum of "slimes" - the present machinery in the Bureau is for pulverizing rather than grinding. This is especially important in obtaining close control of uniform size distribution for mineragraphic investigations.

The new method of boric acid/lithium fluoride fusion will be used for total sample attack.

Further details of atomic absorption instrumentation, techniques and developments will be given at the Fifth Australian Spectroscopy Congress in Perth on May 31st - June 2, 1965. This will be attended by the author who also intends to present a paper on solvent extraction techniques in geochemical analysis - particularly for the elements As, Se, Te, Cu, Pb, Co and Ni.