

COMMONWEALTH OF AUSTRALIA.

---

DEPARTMENT OF NATIONAL DEVELOPMENT.  
BUREAU OF MINERAL RESOURCES  
GEOLOGY AND GEOPHYSICS.

---

RECORDS:

---

1964/10



OVERSEAS VISIT TO INSPECT SPECTROGRAPHIC EQUIPMENT IN  
EUROPE AND ENGLAND

---

by

W.M.B. Roberts

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 It may not be published in any form or used in a company prospectus without the permission in writing of the Director, Bureau of Mineral Resources, Geology and Geophysics.

OVERSEAS VISIT TO INSPECT SPECTROGRAPHIC EQUIPMENT IN  
EUROPE AND ENGLAND

by

W.M.B. Roberts

RECORD 1964/10

CONTENTS

	<u>Page</u>
ITINERARY	1
PURPOSE OF TRIP	1
EINDHOVEN, HOLLAND	1
IMPRESSIONS OF THE PW1210 AUTOMATIC SPECTROGRAPH	2
GERMANY	3
ENGLAND	4
CONCLUSIONS	5
METHODS	6

-----

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 It may not be published in any form or used in a company prospectus without the permission in writing of the Director, Bureau of Mineral Resources, Geology and Geophysics.

OVERSEAS VISIT TO INSPECT SPECTROGRAPHIC EQUIPMENT IN  
EUROPE AND ENGLAND

ITINERARY

Holland

Eindhoven. Application Laboratory, Philips Electrical Industries  
from 29.10.63 to 8.11.63.

Germany

Wiesbaden. Didier Metallurgical Works  
from 9.11.63 to 11.11.63.

Oberkochen. Carl Zeiss Ltd  
from 12.11.63 to 13.11.63.

Munich. Süd Deutsche Kalk und Stickstoff Werke, Hart via Munich, and  
Technische Hochschule  
from 13.11.63 to 16.11.63.

England

<u>London.</u>	Geological Survey of Great Britain, and Hilger and Watts Ltd	} from 16.11.63 to 23.11.63.
<u>Oxford.</u>	Department of Petrology and Mineralogy, University of Oxford	

PURPOSE OF TRIP

The principal reason for the visit was to become familiar with the assembly, alignment, and operation of the Philips PW1210 Automatic X-Ray Spectrograph on order to the Geological Laboratory. In addition a week was spent in Germany inspecting installations of the spectrograph which were being used as production control instruments. One day of this week was spent at the Zeiss Microscope Laboratory at Oberkochen discussing the operation of the Zeiss automatic photo microscope. A week was spent in England discussing the Hilger 3 Metre Direct-Reading Spectrograph with the makers, and problems of silicate analysis with members of the British Geological Survey and with the Department of Mineralogy and Petrology at the University of Oxford.

EINDHOVEN, HOLLAND

Eight days were spent at the application laboratory Philips Electrical Industries Ltd, the makers of the PW1210 Spectrograph. During this period the assembly of the machine was studied in the assembly section, and alignment procedures were carried out whilst doing actual analyses on the instrument. Initially tests were carried out on the accurate analytical limits of the instrument and it was shown that it could analyse to 0.2% sodium, magnesium, silicon, aluminium, and phosphorus, with accuracies similar to or better than other methods. All the sensitivity tests were carried out on slags whose overall composition closely resembled a silicate material which will be analysed in this laboratory. The elements at the lower atomic number end on the periodic table were chosen for these tests because they are the most difficult to analyse by X-ray spectroscopy, and if high sensitivity can be achieved in this region of the periodic table, much higher sensitivity will be obtainable for the higher atomic numbers.

Some time was spent learning to operate the spectrograph; mainly on methods of programming specific analytical tasks. On the PW1210 programming can be done two ways; manually by programme panel on the instrument, a straightforward procedure, but somewhat slower than the alternative method - the pegboard method. In this latter system a pegboard is made up for each programme and stored until required, when it is simply plugged into the instrument and the programme is changed completely in a matter of seconds. Although somewhat more difficult to set up, the pegboard method offers a much quicker programme change and helps eliminate errors in programme arrangement.

Some tests were carried out on the long term precision of the spectrograph, by using a series of slags which had been analysed two months earlier and analysing them again for silicon, manganese and calcium. The curves were remade and the analyses carried out on the new curve. In every case the results were identical, even to the spread of points about the curve.

An interesting method of qualitative analysis with demonstrated in these analyses - that of using a ratio of a standard against the unknown. In this method it is not necessary to have a great number of standards, in fact only one standard is sufficient for acid granitic rocks. A curve is constructed using the intensity ratio of standards to unknown against concentration. At least four samples are used for each of the curves and the standard retained for all analyses using these particular curves. The results obtained were highly accurate, and the method is practical because of the fast operating speed of the automatic spectrograph. A complete silicate analysis can be carried out in roughly 20 minutes by this method; allowing for preparation time a sample could be analysed every half hour.

The stable life of the electronic components of the spectrograph was given as from four to five years of constant operation, therefore, in the interests of continuous high precision operation it will be worthwhile considering closing down the instrument after about four years operation and thoroughly checking the circuits for correct operation, replacing those components which prove to be faulty. This may take a week to carry out and is absolutely necessary if continuous accurate operation is to be achieved. It is of interest to note that we are experiencing difficulties with the PW1540 arising from this very reason; the instrument has been in operation constantly for seven years without any major overhaul or exchange of electronic components and it is now not possible to achieve high precision in analysis. However, since the PW1210 will be doing all of our accurate X-ray analytical work it is not worthwhile going to the expense of changing a large number of components to achieve a precision we will not require from the older PW1540, which will in future mainly be used for diffractometry and qualitative spectrometry.

#### IMPRESSIONS OF THE PW1210 AUTOMATIC SPECTROGRAPH

The machine installed in the application laboratory at Eindhoven has been in operation for three years, and aside from failure of some simple electronic components it had operated continually and satisfactorily over this period. No major structural alterations were found to be necessary, although detailed modifications had been made to increase its operating flexibility. The instrument is highly stable and even at excitation of the order of 80 kilovolts, background is so low that for elements above 1% concentration no background correction is necessary. This results in faster analyses. After the programmes have been set up, the instrument is very simple to operate. Its great advantage lies in its fully automatic operation; once the samples have been loaded into the specimen chamber it is possible to design a programme such that after pressing the start button every sample is analysed for every element programmed without any attention from the operator. Every operation necessary, such as changing analysing crystals, voltages, currents, collimators, vacuum delays, count rates, etc. are performed from the programme panel or pegboard, and at no time while

the machine was used by the writer did it fail to fulfil any of the programmed functions. Thus it is possible to start a programme at the end of the day and the machine will carry it out and present the results typewritten out for use the following morning. A computer attachment for the PW1210 is at present on test at the application laboratory, which will enable direct read-out of concentration from the instrument, thus eliminating the necessity of conversion of the digital read-out. This should result in considerable time saving.

#### GERMANY

##### Places visited:

Didier Works, Wiesbaden.  
Carl Zeiss - Oberkochen.  
Süd Deutsche Kalk und Stickstoff Werke - Hart-Munich.  
Technische Hochschule - Munich.

The first commercial installation of a PW1210 spectrograph was inspected at Didier Werke, in one of the suburbs of Wiesbaden. The instrument was being used to analyse refractories, clays and alloys, and although it had not been in operation long the laboratory manager was impressed with its reliability and speed of operation. Because they had no previous experience of X-ray spectrochemical analysis some time was spent in discussing those techniques of analysis which we had found useful in our laboratory. Several methods of specimen preparation were suggested to them which they had not tried and which should be much more efficient than the methods they were using.

They intend to maintain a close contact with us on our work on silicate and other geochemical analyses, and will naturally keep us informed of anything they do in the analytical field with X-ray spectrometry.

A day was spent at the microscope factory of Carl Zeiss Ltd at Oberkochen, where details of the automatic photomicroscope were discussed with its designer Dr. H. Piller. In the course of the discussion and demonstration, it became apparent that the Australian agents for Carl Zeiss were not aware of the highly sophisticated optics which were available for the photomicroscope when they sold us the instrument. Their lack of knowledge probably results from the highly specialised nature of reflected light optics. As a result, the microscope at present in the laboratory has optics designed for biological work, and although these work satisfactorily, demonstrations by Dr. Piller made it apparent that the correct optics radically improve the instrument's performance, especially in polarized light at high magnification. Dr. Piller has agreed to write to the Australian agents and have them exchange our present optical kit for the correctly designed equipment.

Dr. Piller is currently engaged in research into the reflectivity and hardness of minerals, and is designing equipment to measure these parameters under a microscope. An international panel of mineralogists has been set up to advise on this type of measurement, and on microscopic equipment, but to date no decision has been reached about standards for reflectivity and hardness. The chief difficulty is that trace levels of impurities can materially alter both these characteristics.

For the present the Bureau laboratory would have no interest in these measurements in determining mineral species in reflected light. However, when standardization is achieved and the effects of impurities fully understood, the methods may be quite useful. Dr. Piller has promised to keep me informed on the progress of the work and the decisions of the mineralogical panel.

The laboratory of the Süd Deutsche Kalk und Stickstoff Werke is at Hart, about 100 kilometres east of Munich. They have had a PW1210 automatic spectrograph installed for about three months engaged on the routine analysis of ferro-silicon alloys for iron, titanium, calcium, magnesium, aluminium, manganese, silicon and rare earths. The instrument has had no teething troubles and has produced highly accurate and fast results; the output is about 60 separate elemental analyses per hour.

The officer in charge of the laboratory was particularly impressed with the high stability of the instrument and with the high intensity available for excitation, which results from good design, especially in the geometry of the X-ray tubes and specimen layout. For example, a Siemens instrument also used by the laboratory uses a chromium tube capable of a power output of 2 kilowatts, and although the chromium tube of the Philips machine is only capable of 1.3 kilowatts maximum, the fluorescent intensity for any sample is three times greater from the Philips machine than from the Siemens at the maximum tube output.

While in Munich, acting on a suggestion by the staff of the application laboratory at Eindhoven, I visited the Technische Hochschule where Dr. Hahn-Weinheimer has been working on the application of X-ray fluorescence to the analysis of rocks and minerals. She has been using the ratio method to study the distribution of minor and trace elements in granite and considers that this method will replace optical emission spectrometry in geochemical work for elements above sodium and for all but very faint traces. Because so little specimen preparation is necessary, accuracy is high, and the only inaccuracies will be those that derive from the instrument itself. She is working with a Philips PW1540 spectrograph similar to that installed in our laboratory, and finds that the method is slow, but intends to purchase a PW1210 automatic instrument and believes that this will make possible three silicate analyses per hour.

Her investigation into methods very closely parallels ours. She considers that the fusion techniques are too troublesome and time consuming. We have found this to be the case in our laboratory, and have initiated an investigation into the possibilities of using thin films with internal standards. Dr. Weinheimer has tried this also and although she thinks the method is promising, she considers that the simpler ratio method gives the desired accuracy, and the only objection to the use of the method, that of low output, is overcome by the speed of operation of the automatic instrument.

#### ENGLAND

##### Places visited:

Hilger and Watts - London.

The laboratories of the British Geological Survey, London.

The Department of Mineralogy and Petrology - The University of Oxford.

The main purpose of the visit to Hilger and Watts was to discuss the 3-Metre Direct-Reading Spectrograph built for the Bureau laboratory. Some criticism of the results achieved by them on test runs had been made, and it was considered that these criticisms should be discussed in detail with the instrument's designer. The result of these discussions clarified several doubtful points and the designer assured me that the instrument was entirely satisfactory in every respect. He stressed that no major structural changes should be made in the instrument, and said that it was only a matter for this laboratory to devise suitable operating techniques to make the machine operate satisfactorily on those analyses for which it was designed. He admitted that the staff of Hilger and Watts did not have sufficient experience on silicate analysis to exhaustively test the instrument on the very low concentration ranges of certain elements and assured me that the results on the higher concentrations showed that the instrument was structurally perfect.

When asked how long it should take to have the machine fully operative after installation the designer said that it should not take longer than three months. He stressed that if satisfactory results were not achieved we should modify our operating procedures rather than suspect the instrument of malfunction. He was emphatic that if changes were made to the instrument before thoroughly checking our analytical procedures, considerable time would be lost before the machine could be used for analytical work. For example, it has been

found at Pilkington Glass Works, who operate a 3-metre instrument, that variations in packing density of the sample in electrodes can produce errors in intensity. This effect is so marked that the officer in charge of the spectrograph can tell which technicians have loaded electrodes by the variation in intensity of spectral lines from their individual work.

In the event of minor changes in the instrument becoming necessary, an arrangement was made whereby we can write directly to Hilger and Watts rather than the local agents, and any equipment necessary will be forwarded to us immediately by the quickest practical method.

While at Hilgers I inspected their automatic X-ray spectrograph - the "Fluoroprint". This instrument is not a new design, but is merely the old model "Fluorovac" with an added section to make it automatic. The machine is not up to modern electronic design standard - it still uses vacuum tubes throughout and is much larger than the equivalent Philips instrument. One of these instruments has been given on approval to a steel works at Wetzlar, Germany, for twelve months, and while visiting the South German Lime and Nitrogen Works, at Hart, the officer in charge of the laboratory there told me that they had not been able to get the instrument to work satisfactorily, and were therefore intending to purchase a Philips unit.

In the atomic absorption field, Hilgers have several types of instruments in production, but none of them offers any advantages over the model produced by Techtron, Melbourne.

They are doing some research into excitation with furnaces rather than flames with a view to improving the accuracy of analyses; so far this is only in the experimental stage and no definite results have been achieved.

At the British Geological Survey, the X-ray analytical work is being carried out by Mr. J.E.T. Horne, and an assistant. They are currently working on complete analysis of shales by X-ray methods. The analysis is achieved by addition of internal standards and briquetting the ground sample at 10 tons pressure. They have explored the possibilities of various fusion methods and like us, consider them to be too troublesome to be of real value in routine analysis. I discussed with him the possibilities of thin film work which he had tried without success. However after giving him details of the results we have achieved so far he intends to continue on the investigation of this method combining some of our work with a very useful method of thin film production that he has designed. He will inform us of any useful results obtained.

Some time was spent with Dr. J. Zussman of the Department of Petrology and Mineralogy, University of Oxford. Dr. Zussman has been engaged on the analysis of silicate rocks by X-ray fluorescence. He has tried fusion methods, thin films and briquetted samples and considers that the method which shows the most promise is the fusion method in which a heavy absorber is added to make the mass absorption coefficient uniform for all samples. This method is used by the United States Geological Survey and has given reasonably accurate results.

## CONCLUSIONS

Only two instruments of sequential analysis type are manufactured in England and Europe. These are the Hilger Fluoroprint and the Philips PW1210. An automatic X-ray spectrograph is made in the U.S.A. by Applied Research Laboratories, but this instrument only does 9 elements automatically, and if additional are required to take this number to 22, the total cost of the instrument is around £30,000. The big disadvantage from the geological point of view in this type of instrument is its lack of flexibility in automatic operation. It can only carry out automatic analyses on those elements built into its programme, whereas the sequential analyser can automatically analyse all elements from sodium to uranium in batches of 15 per programme. The changing of the programme can be very simply effected in the laboratory in

a very short time without any fundamental changes to the instrument. Another big disadvantage with the Applied Research Laboratory's instrument is that the ratemeter circuit is a direct adaption of that used in the A.R.L. Optical Direct-Reading Spectrograph, i.e. capacitors are charged by the energy derived from the X-ray beam and read-out is effected by discharging the capacitor and recording its charge. This system is not well suited to X-ray measurement; the ideal and more accurate arrangement is to count pulses generated in the counter probes by the incident X-rays as in the Philips and Hilger instruments.

The work done on the Philips instrument at Eindhoven demonstrated four main features that make it very well suited to the type of work it will be called on to perform in the geological laboratory. These features are:-

1. Simplicity of operation.
2. Speed of analysis.
3. Extreme sensitivity.
4. Excellent precision.

Inspection of installations of the instrument in Germany showed that it is entirely reliable.

On the question of stable life of the electronic components in this instrument, some thought should be given to a very complete systematic check of all parts of the instrument after not more than 4 years of operation. This will ensure that the machine retains its original accuracy.

#### METHODS

Most of the spectrographers with whom methods of specimen preparation were discussed held the opinion that the fusion methods were too troublesome to be really useful for routine application. We have experimented to some length on fusion in this laboratory and had also arrived at this conclusion. For certain limited applications the use of the fusion method is very suitable, particularly where only a few analyses are to be made as in the case of work done by Dr. J. Zussman of Oxford University. Besides the length of time taken in fusion methods, the large dilutions involved result in lower intensities for the analytical lines, this is particularly the case where a heavy absorber is added. For the type of application in this laboratory, the ratio method appears to be the most promising. It has the advantage of constantly checking the machine variations as well as taking full advantage of the automatic operation of the PW1210. Some dilution with a heavy absorber may improve the analysis because less standards may be required as the matrix approaches a common mass absorption coefficient. At this stage however it is not considered advisable or practical to dilute the sample to such an extent that a common mass absorption coefficient is actually achieved, but rather to combine the ratio method with a 1 x 1 dilution with a heavy absorber during the grinding process to improve the standard of accuracy.