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DEPARTMENT OF MINES AND TECHNICAL SURVEYS

GEOLOGICAL SURVEY OF CANADA

TOPICAL REPORT NO. 72

1. VISITS TO UNIVERSITY AND GOVERNMENTAL SPECTROGRAPHIC LABORATORIES AND SPECTROGRAPH MANUFACTURERS IN THE EASTERN UNITED STATES, June 11 - 23, 1962.

2. THE TENTH COLLOQUIUM SPECTROSCOPICUM INTERNATIONALE AT COLLEGE PARK, MARYLAND, June 18 - 22, 1962.

BY

W. H. CHAMP

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Introduction

The main reasons for making this trip were:

1. To evaluate and compare features and specifications of spectrographic equipment in current manufacture.

2. To study techniques of excitation and sample handling in the analysis of inorganic materials by direct reading optical emission spectrography.

The opportunity to combine this with attendance at the Tenth Colloguium Spectroscopicum Internationale held near Washington, D.C. made it possible to establish or renew personal contact with a large number of research scientists and technical personnel.

(June 12-13) Cabot Spectrographic Laboratory, Massachusetts Institute of Technology, Cambridge Massachusetts.

This is a teaching laboratory and it is not yet concerned with direct reading apparatus. I took the opportunity to renew my acquaintance with Professor W.H. Dennen and to discuss analytical problems generally with him and some of his graduate students. He is presently carrying out some tests to determine whether small displacements of band systems in emission spectra can be related to variations in isotope ratios in certain mineral species.

R.F. Jarrell's original Wadsworth spectrograph is being reconstructed as an exercise by the students. This was the (1939) prototype of our spectrograph and I was interested to know what

arrangements had been planned for the interchange of gratings, but this information was not available.

In discussion Dennen mentioned a technique which might be of some interest to Dr. C.H. Smith. A grinding wheel was mounted on a bench in such a way that a ten foot length of drill core could be passed across it and the grindings caught in a pan. By grinding a slight flat edge along this length you effectively average it, and the resulting sample is not contaminated except by a small quantity of alumina from the wheel. If spectrographic analysis shows anything of interest the rod can then be broken up and analyzed in detail.

(June 12) Research and Control Instruments, Woburn, Mass.

This is a new company started by a small group of scientists well known as individuals, who are rapidly becoming known as a company (many ex Bausch and Lomb). Mr. H.J. Levesque, in charge of sales, showed me through the entire plant, describing the manufacturing facilities, etc. and showing various spectrograph models under construction. They have a Hg monitor system similar to that of Jarrell-Ash, which makes the direct reading spectrograph somewhat less dependent on laboratory temperature (see later comment). A.T. Myers of the U.S.G.S. laboratories at Denver has a spectrograph under construction, with about 40 fixed-position photo tubes. Many people are waiting to see what results he gets with it. (I discussed this with him later). However, I was not happy about the apparent inflexibility of the photo

tubes. Dr. J. Saunderson, RCI president, explained to me the whole process of alignment of exit slits and photo tubes, which is quite complex. However, when I asked about altering the wavelengths used he stated this was not intended to be done outside the factory. In my opinion this is the one objectionable feature which makes an otherwise excellent instrument not suitable for our purposes.

(June 13) Baird-Atomic, Inc., Cambridge, Massachusetts

Mr. R. Roy, sales manager, conducted me through the section of the plant devoted to spectroscopy and demonstrated various spectrograph models. Their 3-meter research model direct reader is very flexible, with interchangeable photographic and photoelectric recording. A removable direct reading head unit contains up to 20 pre-aligned photo tubes. More than one could be used of course, making a complete change of program a matter of about fifteen minutes. In a laboratory such as ours where routine and special analyses occur at random more or less, this is a most advantageous feature. The geometry of the instrument would also suit our restricted quarters and in general this instrument would seem to fill our requirements rather well. Individual phototubes can be reset without much difficulty. It is conceded by most people that BA have the best Hg monitor correction system for direct readers. They were first to patent the idea and other companies have less efficient copies. The system corrects spectrograph alignment for moderate temperature changes which are not to rapid. It is still

recommended however that the relative humidity in the laboratory be maintained at not over 50%.

The prototype for the new "Kopito" furnace was also demonstrated. Controlled electric currents are passed through special graphite cloth heating elements which are raised to more than 6000 deg. F. in seconds. Samples of almost any material placed on the heating element can be melted or boiled rapidly. The uses are innumerable. My immediate thought was to volatilize mercury from fairly large (10 gram?) samples of soil or rock, etc. Probably the best way to determine Hg at the ppb level would be the atomic absorption method, using a furnace such as this with an appropriate spectrophotometer and Hg hollow cathode tube source.

(June 13) Jarrell-Ash Company, Newtonville, Massachusetts

Mr. Stanley Smith conducted me on a tour through the manufacturing plant and described the features of various models of spectrographs under construction. Mr. J. Dunn had been unfortunately called out of town, so I was unable to discuss with him certain aspects of grating installation in the Wadsworth spectrograph. Mr. Boyd Fagan of the analytical division discussed with me some instrumental problems and possible reasons for difficulties we were having with our densitometers. (These were later resolved, having been caused by the effects of certain tube substitutions.)

Probably the most flexible and useful spectrograph for analytical purposes is the Mark IV Ebert convertible direct reading model. With this instrument any project conceivably of interest to the GSC laboratory could be tackled. It is however large and relatively expensive. The smaller "Atom counter", a 1.5 meter spectrograph, is also quite flexible. It has the advantage over the similar RCI model that while it will also take upwards of 40 phototubes, each can be individually reset in the laboratory without undue difficulty. It is usually equipped with a sequential read out system which can handle either 11 or 22 elements per exposure. Providing the required phototubes have been installed, re-programming is a matter of switching connections and can be done in a few minutes. The entire package is very neat and convenient and relatively inexpensive - about $25,000. Mercury monitors are included and direct reading spectrographs are less temperature dependent, supposedly, than they were some years ago.

(June 14-15) Spex Industries, Inc., Scotch Plains, New Jersey

Mr. D. Landon showed me through the plant and also demonstrated various pieces of Spex equipment. With him and Mr. A. Mitteldorf, president of the company, I was able to discuss sample handling and excitation problems at length. They have a new version of Strasheim's electrode loader in production, but after trying it out I do not think it is any better (probably not as good) as the simple apparatus we now use. They are also promoting the sales of "premixed and loaded into capsules" weighed charges of graphite and buffer, etc.

to customers' specifications. But we use such a variety of methods that this would not save us much time, and importing these from the U.S.A. would be rather expensive.

They are now selling the "Shatterbox" which is their improved version of the European designed "swing mill". It is a very fast, rather noisy, but efficient means of pulverizing rocks or similar material to very fine particle size. It is of course still subject to metal pickup to some extent as are all such devices, but its speed and ease of cleaning, and the larger quantities it will take compared to the "paint shaker" apparatus make it worthy, in my opinion, of purchasing for our sample preparation section.

We discussed the jet-controlled D.C. arc in detail. The Spex "Stallwood" jet has been modified several times but is still in my opinion not designed to accomplish the functions originally intended. It does however work very well, with an added quartz dome, as a controlled atmosphere chamber for the arc. We are modifying our own jet-control slightly so that this feature can be more conveniently utilized. The idea of the added dome was originally proposed by Dr. Denis Shaw. I agreed to supply a written account of the development of the Stallwood jet control, which was subsequently published in the "Spex Speaker", and also in "Canadian Spectroscopic News".

The convertible feature of the Ebert spectrograph consists of a motor driven mirror which is lowered into place at a 45 degree

angle to divert the dispersed radiation from the photographic plate to the bank of phototubes. Apparently some people have had a great deal of mechanical trouble with this. On the other hand, Dr. S. Berman at NRC says this is a simple and efficient device. Doubtless the availability of service facilities is a factor of considerable importance.

(June 15) Department of Soils, Rutgers, the State University, New Brunswick, New Jersey

I visited the spectrographic laboratory and discussed some analytical problems with Mr. J. Gamble and Mr. A. Bedrosian. Their equipment is similar to ours. They are testing the relative merits of various wet and dry ashing procedures for grasses and leaf samples. They have done some work with the Spex jet and general semi-quantitative methods. They think, as do I, that there is a good possibility of being able to determine trace elements by arcking air-dried and crushed plant matter directly. I think this could be done by using a relatively large sample with an appropriately modified jet control in a nitrogen-free atmosphere.

(June 19) U.S. Geological Survey Laboratories, Washington, D.C.

(1) The laboratory at the Naval Weapons Plant was visited and a description of the equipment given by Miss Helen Worthing. This laboratory under C.L. Waring, and the one at Denver under A.T. Myers, are using a simplified system of reporting semi-quantitative analyses

on a fixed number scale of six steps. This is practically the same as the system we have recently established. The variety of equipment which they have to apply to a wide range of analyses is most impressive, though they are not happy about the resultant over crowding of the available laboratory space. They have an Ebert direct reader with a clock type read-out system, which does not seem to me to be warranted in a non-industrial situation.

(2) The X-Ray laboratory in the General Services Administration building was also visited. Mr. Harry Rose described the ARL X-Ray Quantometer and outlined sample preparation and briquetting practices. In X-Ray fluorescence analysis variations in sample matrix usually cause considerable fluctuation in observed intensities because of large absorption coefficients for the light elements. By adding lanthanum oxide, itself a strong absorber, to the fusion melt this "matrix effect" is diminished, in a way similar to the use of buffer materials in spectrographic analysis. The working curves obtained show excellent precision and make possible the analysis of major elements in a wide variety of silicate rocks with accuracy comparable to the best chemical analysis. This procedure however is not directly applicable to trace elements determination.

The electron microprobe, constructed in this laboratory was also demonstrated by Dr. A. Tousimis.

(June 20) U.S. Bureau of Mines Laboratory, College Park, Maryland

A short visit to this laboratory was made. Mr. M.J. Peterson showed us an impressive array of equipment. The laboratory is quite crowded. They have recently obtained a plasma jet solution analyzer, which was demonstrated, but they have not yet had time to put it into use.

(June 21) U.S. Department of Agriculture, spectrographic laboratory of the Plant Industry Station, Beltsville, Maryland.

Dr. A. Specht, showed us the laboratory and discussed their procedures. They have a Baird direct reading spectrograph, set to determine ten elements of interest in plant materials. They are quite satisfied with it. Each day standards are run and corrections made for each element if needed. It takes about six months experience before an operator becomes used to the operation of the machine and can tell by the daily check whether adjustment or corrective maintenance is required. They estimated it took about one year after installation before they had the instrument running routinely - but this may have also included development of methods. They use a solution procedure (on which I have notes) which seemed to me rather laborious, but is apparently effective. Two people work continuously on this one plant analysis project, but they were reluctant to provide any figures on the actual output of determinations. Baird's monitor system works well and small temperature variations present no problem, but it is

necessary to keep relative humidity below 50%, which is sometimes difficult for thim in the summer.

(June 23) Pennsylvania State University Spectrographic Laboratory, State College, Pennsylvania.

Mr. N.H. Suhr showed me through the laboratories in the Mineral Sciences Building. They are very well equipped and probably have a budget equal to that of the GSC. They had recently received a very large Japanese electron microscope, which was their second one. I was shown the Applied Research Laboratories electron microprobe in use, with which they are quite satisfied, but with the roomful of accessories which are required it must be exceedingly expensive.

With Mr. C.O. Ingamells we discussed some of the problems involved in production of standard samples. They volunteered to supply a sample of lignite ash to the Canadian Association for Applied Spectroscopy if the Standards Committee wished to have it. Also Mr. Ingamells supplied me with a small amount of a standard granite sample "GR" which was prepared by the Petrological Research Institute at Nancy in France. It is not certified for trace elements, however.

Their spectrographic laboratory uses our jet control design for the D.C. arc, which they obtained from Mr. O. Joensuu some years ago. Their methods are similar, but they have also done

considerable work with nitrogen-free atmospheres. For volatile elements they have obtained a Spex model jet which when used with 1/4" electrodes in an argon-oxygen atmosphere enables them to determine such elements as zinc at the one p.p.m. level. We expect eventually to have similar methods in operation.

Some work had been attempted in infrared investigations of minerals but the scientist concerned was no longer there and since results were apparently disappointing the work had been discontinued and they could give me no information of any interest.

The Tenth Colloquium Spectroscopicum Internationale, University of Maryland, College Park, Maryland, U.S.A.

This international conference, held June 18 to 22nd, 1962, was the first of the series to be held outside Europe. Its main purpose was "to provide communication between spectroscopists throughout the world in order to make known the most recent advances in research in both fundamental and applied spectroscopy". Events and program were very well planned and at no previous meeting have I been able to meet and talk with so many people from so many parts of the world.

The meeting was sponsored by the Society for Applied Spectroscopy (USA), the Department of Chemistry of the University of Maryland, and the Commission on Spectrochemical and Other Optical Methods of Analysis of the International Union of Pure and Applied Chemistry. My copy of the program is available to anyone interested.

Abstracts were published in Applied Spectroscopy, Vol. 16 No. 2 for 1962, and a three volume set covering the whole proceedings will soon be obtained by the GSC library.

There were 24 invited papers by various internationally known authorities plus over 100 contributed papers on all aspects of spectroscopy. There were 34 instrument exhibitors booths set up in a separate large building. This was actually a bit disappointing in spite of its size in that it was mostly American and not as much European apparatus was on exhibit as I had hoped to see. The registration was about 1000 people from 28 different countries. The Canadian representation was very good and I was able to renew contacts with a number of people who do not regularly attend our Ottawa Symposia.

There has been a resurgence of interest in excitation sources and the properties of various controlled arcs recently, mainly in connection with high temperature research, and some interesting analytical possibilities arise in this connection.

Dr. B.J. Stallwood unfortunately was not present, having suddenly left to accept a new research position in California with Northrop Space Laboratories. However, two of his colleagues, F. Moore and K. Thygesen presented a paper on their work entitled "Arc Source for Third Spectra". This described modifications to their special "jet-enclosed arc" by which they were able to obtain the third spectra of Cu, Fe, V, Mn and Co with some indication that fourth spectra might also be

obtainable in certain regions of the arc at very high temperatures.

Both Spex Industries and National Spectrographic Laboratories displayed models of the "Plasma Jet" Solution Analyzer. This is another related controlled arc in which the sample vapour is carried into the discharge zone of the arc by a swirling stream of helium. It is a high temperature source (about 8000°K) capable of great precision in the analysis of almost any type of solution. However, because of the relatively high background continuum it is not particularly applicable to trace element analysis. Louis Owen of Goodyear Atomic, one of the first workers with this device, gave a paper on "Spectral Excitation of Uranium Hexafluoride for Isotopic Assay with a Stabilized Plasma Jet", in which the properties of this excitation source were described in detail. These two papers in particular, plus a number of others on similar related subjects, gave rise to a great deal of informal discussion on arc excitation processes which I found most interesting and valuable.

Jarrell-Ash company had on exhibit a model of an "Optical Maser Source" which seems to have potential application in microanalysis. A narrow beam of nearly monochromatic radiation in the infrared or visible range can be focused on an area as small as 50 microns. The resultant heat will vaporize the material at that point, which can then be excited by passage through a spark gap and recorded by a spectrograph in the usual manner.

The atomic absorption method of analysis, at least as described in a paper by A. Walsh, would appear to have rather limited application to our type of work at present. Unless very complicated equipment is designed you can only do one element at a time, since a hollow cathode tube source is needed for each element. It is also necessary that the element be vaporizable and stable in the flame column. But for certain special applications great sensitivity can be obtained, with relatively little interference or matrix effects.

A few points of interest brought out in discussions with various people follow -

Mr. O. Joensuu, Marine Laboratory, University of Miami, showed me some comparative analyses he had done in cooperation with Danielsson of Sweden. He had sent a group of twelve samples as complete unknowns for analysis with the tape machine. The results were compared with Joensuu's values, obtained with jet-controlled D.C. arc in a CO_2 atmosphere. For both major and minor elements agreement was excellent in almost every case.

Mr. A.T. Myers, USGS Denver laboratory, observed that contamination with barium in grinding in the paint-shaker apparatus could be avoided by using grinding balls of 99% Al_2O_3 composition instead of the lower grade. They do not need to be perfectly round. Further information may be obtained from Mr. Charles Ryland, Coors Porcelain Plant, Golden, Colorado. We also discussed the direct reading spectrograph being built for Myers by RCI. He intends to use

this for semi-quantitative survey type analysis only, at the lowest trace element concentrations - about one ppm. I have his list of 36 trace elements to be determined. The method or methods are not completely established yet but it may be optimistic to expect to use any single general method at such low limits - however, the accuracy expected was not stated.

Mr. E. Vejvoda, Dow Chemical, Denver, makes the point that because of the speed of making excitation and volatility tests, etc. on a direct reader it is often more convenient to develop a method in this way and transfer it to the photographic instrument. Their analytical problems, as ours do, require the use of both photographic and photoelectric recording spectrographs.