HW-12539

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1. D. W. Pearce
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3. T. W. Hauff
4. W. A. Briggs
5. H. R. Schmidt
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D. W. Pearce
METALLURGY AND CONTROL DIVISION

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This Document consists of 20 Pages

RE: TRIP REPORT

The following trip report covers the writer's recent visit to Pittsburgh, Schenectady and Oak Ridge.

At Pittsburgh, the writer attended "The Fourth Annual Analytical Symposium". At Schenectady, he visited personnel in both the Research Laboratory and K.A.P.L., to discuss a number of problems. The visit to Oak Ridge included discussions with various technical people at the three sites.

For purpose of convenience, the report is drawn up in ten separate sections, these being as follows: "Pittsburgh Analytical Symposium, Mass Spectrography, 706-D Process, Redox Analyses, Fission Counting, X-Ray Photometry, Fluorimetry, Fluoride Determination, Distilled Water Systems and Personnel".

A. H. Bushey
Analytical Section
Metallurgy & Control Div.

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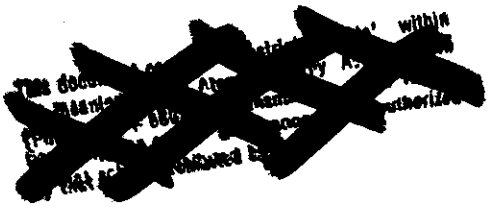

PITTSBURGH ANALYTICAL SYMPOSIUM

The Pittsgurgh Analytical Symposium was the most satisfactory technical meeting that the writer has ever attended. The subject matter of papers was of considerable interest, the material was well presented and the display of scientific materials and instruments was of value. Following is a brief abstract of the most pertinent papers:

Professor I. M. Kolthoff discussed a means of chemical analysis based on reaction rates. Systems having two components that react similarly with a given reagent are treated with an excess of that reagent and the extent of net reaction determined after several suitable time periods. The results are calculated with the aid of the predetermined reaction rates of the separate components. The reaction rates of the separate components should differ by more than 3 to 1. The method bears a marked similarity to radio assays of mixtures containing several active elements. Examples cited by the speaker included mixtures of carbonyl compounds and mixtures of compounds containing internal and external double bonds.

Another subject discussed by the speaker was the effect of induced reactions on analytical problems. In particular, he discussed the reaction involved in the determination of hydrogen peroxide with ferrous iron. In the presence of oxygen, the ferrous titration increases with increasing alcohol contamination of the solution; this is due to an induced oxidation that consumes iron. Conversely, in a nitrogen atmosphere the iron titration decreases with increasing alcohol content; this results from an induced reaction that consumes peroxide.

A similar situation exists in the reaction between ferrous iron and persulphate and, to a small extent, in the iron-permanganate reaction.

An interesting paper by Nader and Frediand of Merk and Company discussed a method for evaluation of the amount of an isomeric impurity present in an organic compound. The method is based on the increased solubility of the compound plus isomer in a solvent as a result of the presence of the latter. A suitable solvent is one that is saturated by 0.5 to 7% of the compound, that undergoes no reaction with the solvent, is pure and is moderate volatile. The solubility of the compound to be tested in this solvent is determined; if it is greater than that of the pure compound, as independently established, impurities are indicated.

Dr. William Mac Nevin of Ohio State University discussed the separation of rhodium and iridium by means of the controlled cathode potential technique. The apparatus employed was that described by Lingane. Rhodium alone precipitates at -0.3V and iridium alone at -1.0V. A mixture however, can not be separated unless iridium is oxidized to the tetravalent state, all foreign complexing agents are destroyed and the solution is 3.5% to ammonium chloride.

The speaker indicated that it is, in general, best in employing this technique to start the electrolysis at a low potential and increase the latter gradually to the desired value. He pointed out that chlorine must be absent to avoid the consequent attack on the electrodes. Its presence is avoided by adding hydroxylamine to the solution.

Dr. V. A. Stenger of Dow Chemical Company described a method for separating cesium from other alkali metals. The method promises to be of considerable value to us at Hanford. It is based on the relatively high solubility of cesium bromide in free bromine as indicated by the following table:

Bromide Salt	Solubility in Bromine
Lithium	.005 g/100 g
Sodium	.009
Potassium	.0185
Rubidium	.058
Cesium	18.3

In one example cited 0.0095 g. of cesium bromide was recovered by a single seperation from a mixture containing 0.0100 g. cesium bromide and 0.200 g. of potassium bromide.

Dr. Stenger distributed free samples of cesium bromide purified by the above separation and indicated that Dow is looking for other outlets for material.

Stakowski and Freiser of the University of Pittsburgh reported the successful application of isquinoline to the determination of divalent metals, copper and zinc in particular. If the sample solution is first treated with an excess of thiocyanate and then with isquinoline, a precipitate of the general formula $M(CNS)_2 (IQ)_2$ is formed. The copper salt precipitates at pH of 2.5 to 3.0. The salts of both copper and zinc precipitate at pH of 6.5 to 7.0.

The zinc salt may be dried at 110° C; it has a gravimetric factor of 0.1486. In making precipitations the author used 0.5M thiocyanate and 0.2M isoquinoline, the latter being 70% neutralized with hydrochloric acid. Over a wide range of zinc contents, an average error of only 0.02 mg. of zinc was reported.

Eleven exhibitors took part in the exposition of analytical tools. The new simplified Beckman Spectrophotometer was on display; the instrument is well designed, simpler to operate than the present more versatile unit and well suited to routine applications. One item in line with all three comments is the arrangement whereby the sensitivity control and slit width adjustment are combined into a single control.

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Fisher Scientific Company displayed a "Grammatic Balance Magnifier" (No. 1-910-10), a small unit with a lens that greatly aids in reading the vernier and rotating scale on the Mettler Balance.

A novel idea in connection with a constant temperature bath was shown by one of the exhibitors. Heating was supplied by an infrared lamp located outside the bath and connected to the thermostat relay; the lamp shown on a large black screen in the bath, thus producing a mild heat, distributed over a large area.

The writer talked with Mr. R. Halvorsen, an aquaintance who has interest in a small instrument concern known as, Parker Halvorsen. He described an automatic titrator being developed. It contains a light source impinging on a photocell; the sample, containing a suitable indicator, is placed between these and the proper color filter placed in the light path. The titration is started and will continue until the indicator color change affects the transmitted light to a predetermined extent sufficient to automatically close the buret.

Halvorsen also further described a patented process for making extremely fine (less than 10A) alumina and expressed his desire to find an outlet for the material.

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MASS SPECTROGRAPHY

One of the major problems facing the Hanford Analytical Section at the present time is that of the determination of concentrations of heavy metal isotopes; these include uranium and the trans-uranic elements. The writer discussed this problem with many people at Schenectady and Oak Ridge. It was apparent from these discussions that we must clarify our problems before we can make any progress on the subject. Detailed information is needed on the nature of the samples to be analyzed, their composition and concentration range and the desired precision of analyses. No intelligent selection of analytical methods can be made without having this information at hand.

On January 26 the writer had a conference with G. M. Foust, J. G. Hutton and J. G. Neuland of the General Engineering Laboratory and F. J. Norton of Knolls. In particular the conference concerned eight Analytical Mass Spectrometers currently being built by the Engineering Laboratory. Seven of these are contracted for but the eighth is not. This instrument is complete except for the head and the case; it was pointed out that with this degree of completion the unit is ideally suited for investigations of a suitable source for handling relatively non-volatile samples. Mr. Foust agreed, at my request, to hold this instrument for one month so as to permit us time to determine our need and to institute authorization through regular channels if we require it. The samples to be analyzed at Hanford are non-volatile and considerable experimentation may be necessary to design a compatible mass spectrograph source. In view of this Mr. Foust pointed out that this investigation might be most expediently done at Schenectady and suggested that the problem could be started at once if we would finance it.

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The question of obtaining an ion source from our non-volatile samples will require investigation. Several methods are available. The sample may be volatilized at high temperature from a small furnace or from a hot wire within the source enclosure. With the hot filament technique it should be more simple to devise a source to permit handling of multiple samples without breaking the vacuum between each. However, the hot filament cannot be expected to produce as uniform volatilization rate as the hot furnace. The most desirable method for making measurements is to scan the mass range, this requires a constant ion beam and, consequently, a uniform feed of gas. It might be possible to develop the hot wire technique so as to obtain direct ion emission and so eliminate the electron ionizing beam; however, the same limitation applies with regard to uniformity of volatilization.

The majority opinion on type of source, favored prior chemical conversion of the elements to a relatively volatile compound. This opinion results from the successful experience with uranium fluoride and from the fact that there is limited knowledge on handling of solid samples.

The conversion of uranium to the fluoride is carried out in the Oak Ridge laboratories with ease and dispatch. The sample is converted to the oxide and heated in a vacuum system with CoF_3; the UF_4 driven from the mixture is condensed in a cold trap. None of the technical people who discussed this problem with me had information regarding the behavior of the trans-uranic elements under this treatment. Use of this procedure poses the rather difficult problem of obtaining free fluorine for refluorination of the cobalt compound.

F. W. Hurd at K-25 has initiated an investigation on the formation and use of uranium chloride for isotope studies with the mass spectrograph. Free chlorine is an unsuitable chlorinating agent because it forms the non-volatile UCl_6. Carbon tetrachloride and propylene dichloride will produce UCl_4 which is sufficiently volatile. As a note of caution, mercury pumps may not be used with the instrument if chlorine is present because HgCl has a molecular weight identical with that of U^{235}. No information was obtained on the volatility of the chlorides of the trans-uranic elements. The above suggests the necessity of making a literature search, and perhaps laboratory investigations, leading to selection of compounds of trans-uranic elements that can be employed in a similar manner. Such a compound should not contain elements in the anion that have several isotopes since this would confuse the mass spectrogram; iodide fulfills this requirement but has the objection of high mass.

Drs. Kanne and Hurd both expressed the opinion that the limiting sensitivity to be expected from mass spectrographic analysis is about 0.1%. Presumably this limit could be lowered slightly if an ideal feed compound could be selected and if interfering masses are absent. The presence of high activity in the sample might affect the ionizing, focusing or collecting systems so as to raise this limit. Another point made by Dr. Hurd is that certain compounds will tend to produce greater "memory" effect than others.

Dr. Norton predicted that we should have little trouble in setting up and operating a G.E. mass spectrograph with the conventional type of sample. He stressed the desirability of having several technical people gain prior experience with the instrument and of having two instruments on hand to facilitate handling different types of samples

and to permit operation during repair of one of them.

Dr. Hurd quoted his experience with the original G.E. spectrographs received at K-25; these required heavier duty components and more efficient evacuation systems.

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706-D PROCESS

At the X-10 site in Oak Ridge, the writer discussed the captioned process with Messrs. Kelly and Wyatt. The process is completely described in reports available at Hanford. It consists briefly of addition of lead, precipitation of combined lead and barium sulfate, conversion to carbonate and then to nitrate. Lead is removed electrolytically from the solution and barium successively precipitated as the nitrate and chloride from strong acid solution.

Analyses currently made at Oak Ridge to support the process include the determination of barium in the original solution and in the electrolyte after lead separation. Further barium determinations are made upon each of the waste material obtained throughout the process. Additional determinations include uranium in the original dissolver solution and residual lead in the electrolyte.

Barium is determined by adding barium carrier and making three successive precipitations of barium chloride from an ether-hydrochloric acid solution. The residue obtained is weighed to determine the recovery and is then counted according to standard techniques. Uranium is determined by the salicylate color method, and lead is determined by the dithizone color method or alternatively by polarographic means. It was reported that the methods are satisfactory and that good material balances are obtained. Several of the waste solutions contained suspended matter so that no satisfactory aliquot could be obtained from them; in these cases the practice is to estimate the total volume of the sample and dissolve it completely in nitric acid. The solution is made to one liter and suitable aliquots taken from this for analysis.

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The main problem involved in the determinations, and one that will require considerable attention if the process is installed at Hanford, concerns the high activity. The laboratories in which the determinations are made at Oak Ridge were not designed for the purpose and are reported to be unsuitable in many respects. It is necessary to have many of the operations performed behind heavy shielding that completely protects the operator, thus remote control technique must be highly developed. The principal operations to be handled in this manner include the initial sampling, the subsequent dilutions and the barium chloride precipitation steps. In addition, since uranium is determined on the dissolver solution, these operations must be conducted with adequate protection.

REDOX ANALYSES

Pu by TTA

There has been considerable investigation at KAPL on the determination of Pu by the TTA extraction procedure; Dr. Cefola has carried out the major part of this work. During a discussion, he stated he plans to visit Hanford in the near future to examine our methods of handling active solutions.

In brief, the procedure employed in this determination is as follows: Adjust 10 ml. of sample to approximately 0.25M HNO_3; higher concentrations may be satisfactory but the value must be above 0.1M to avoid hydrolysis of uranium. Make the solution about 5 X 10-4M. to $K_2Cr_2O_7$; this addition has been found to promote complete Pu recovery. Add hydroxylamine to reduce Pu to the tri-valent state and add dichromate or nitrite to oxidize to the quadrivalent ion. Nitrite has been found to be the more desirable of these reagents. Add an equal volume of 0.08 M TTA in benzene and extract the Pu. Evaporate an aliquot portion of the benzene phase on a counting plate and determine the alpha count.

Americium follows the Pu in this separation and may be the source of appreciable error. Curium is likewise extracted as well as about one-half of the fission products.

Only quadrivalent Pu is extracted. In a series of experiments Dr. Cefola stated that 95.4% Pu recovery was obtained but that no definite initial steps had been taken to assure that Pu was entirely in the +4 state. He indicated that 95-96% recovery had been obtained by the lanthanum fluoride procedure. Uranium did not appear to interfere with the recovery. Hexone solutions were analyzed with similar accuracy by first extracting the Pu into dilute nitric acid.

Dr. Cefola referred to his observation that hexone interferes with the lanthanum fluoride method for determining Pu. We recognized a similar effect at Hanford but subsequently discovered that high nitric acid content rather than hexone was the cause of the difficulty.

Experimental work at KAPL has dealt primarily with the effectiveness of the TTA method in separating quadrivalent Pu from a mixture. The writer pointed out that Hanford's interest also includes the determination of total Pu. Dr. Cefola indicated he would give more attention to this problem.

Nitric Acid in UNH

At KAPL a considerable amount of time has been spent in attempting to perfect a method for this determination. Dr. Rider referred to the many approaches to this problem and the many reagents for complexing uranium that had been investigated. His conclusion is that the presently employed oxalate procedure is the most satisfactory one known.

Aluminum

Until recently aluminum determinations have been made at KAPL by an acidimetric procedure. To avoid interferences the determinations are now made gravimetrically using a mercury cathode separation and precipitation with oxine. Dr. Rider was interested to learn of our modified acidimetric procedure.

Dr. Grimes at Y-12 in Oak Ridge described a procedure for determining as little as 5 ppm aluminum in uranium. An outline of the procedure is as follows: Dissolve 0.1 g of sample and add 10 gms. of Na_2CO_3, add oxine and extract three times with chloroform. Combine the

chloroform portions and extract aluminum into an aqueous solution of 5% H_2SO_4 and 5% acetic acid, adjust to pH 3.0 with ammonia gas. Add oxine and extract three times with chloroform; this removes iron and copper but not aluminum. Adjust the aqueous solution to pH 4.5, add oxine and extract the aluminum into chloroform. Adjust the volume of the latter to 25 ml and determine the light absorption with a photometer, using a 395 mu. filter.

Ruthenium

Dr. Rider reported considerable success in separating ruthenium by electrolysis, a controlled potential unit was employed in this work. Since ruthenium is about the only fission product that is reducible, it is probable that the separation could be effected with a simple electrolysis unit. The chemists have returned to the use of platinum discs as cathodes to avoid corrosion problems associated with the use of more common metals. Since ruthenium cannot be removed from these discs the latter are made of very thin gage metal and are used only once.

Uranium

Until recently, high concentrations of uranium have been determined at KAPL by a polarographic procedure. Recent tests have shown that the precision obtained is frequently greater than 5%. As a result this procedure has been discontinued in favor of the volumetric one.

FISSION COUNTING

The question of the desirability of having a fission counter at Hanford is similar to that regarding the mass spectrograph. The first step is to review the separate problems involving isotope determination and establish the nature of the samples, their composition, their approximate concentration and the required analytical precision.

W. R. Kanne was of the opinion that plutonium isotope abundance could be determined by a combination of chemical analysis, spontaneous fission counting and alpha pulse determinations. The presence of interfering isotopes of other elements could introduce many complications in this scheme. Concerning the need for this determination, Dr. Kanne asked if information relating pile power level to concentration of isotopes were not already available in the project literature. He also strongly recommended that we discuss the problems of chemical determinations of trans-uranic elements with Dr. Manning at Chicago.

At K-25, the induced fission counter is employed on a routine basis and provides a convenient and accurate means of analysis. F. W. Hurd demonstrated the steps employed in making an analysis and discussed problems that would arise in handling hot solutions. He pointed out that separate rooms are required to house the neutron irradiation chamber and the measuring panel; neutron radiation was sufficiently strong to make it necessary to remove counting instruments from the latter room to another part of the building.

X-RAY PHOTOMETRY

The X-Ray photometer employed at Hanford is one that was designed by General Electric particularly for the determination of lead in gasoline. For this application, large size solution cells are employed and the aluminum window on the cells is quite thin. In employing the in-

strument at Hanford we must use a relatively small volume of liquid. As a consequence, the length of path of the light beam in solution is shorter than desirable. In addition, there is constant danger of denting the thin aluminum window.

The writer discussed this subject with Messrs. Moles, Liebhafsky and Wendslow at Schenectady. The former indicated that General Engineering Laboratory would be interested in working on this problem and believes it not to be too difficult to solve. In this connection he suggested that if Hanford were to make funds available for this, research work could be started immediately. There was no positive reaction to the writer's suggestion that the investigation be jointly financed by Hanford and the General Engineering Laboratory.

Another factor that has tended to cause the instrument to give somewhat erratic results is the lack of uniformity of the phospor screen. Mr. Moles gave the writer a new and more uniform phospor and asked us to try it on our instrument and let him know our findings regarding it. The screen is manufactured by the Patterson Screen Division of Du Pont.

FLUORIMETRY

Dr. Rider indicated that the fluorimeter designed and built at Schenectady has given excellent service. It has been in routine operation 16 hours per day for three months without attention other than normal servicing. The instrument is simple in design, convenient to operate and has high sensitivity. The normal blank is equivalent to 0.7 ug of uranium, this giving a scale reading of 70 at maximum sensitivity setting. Uranium in concentrations of 0.06M or less is determined directly on a sample with an average precision of about 10%. Concentrations in the range 0.000XM are determined with an average pre-

cision of about 20%. Blue prints of the design are in the Hanford files.

FLUORIDE DETERMINATION

The determination of small amounts of fluoride in connection with the 234-5 program has given some difficulties here. In this connection it was of interest to learn that such determinations are made at X-10 by the conventional color titration technique. The operators reported that 0.1 ug of fluoride can be determined and that 1 ug. can be measured to within approximately 10%.

DISTILLED WATER SYSTEMS

While in Pittsburgh the writer called the Aluminum Research Laboratories of the Aluminum Company of America at New Kensington. In a talk with R. H. Brown, head of the Corrosion Division, we discussed application of aluminum piping for distilled water systems. Mr. Brown confirmed the writer's opinion that aluminum pipes are widely used for such purposes. He quoted figures showing that there is little contamination of the water. He recommended 3S aluminum alloy for diameters less than one inch and 63ST-5 alloy for the larger sizes. The distinction is one of cost. Valves are commonly made of either 43 or B214 alloy. Depending on the mechanical properties desired the storage tanks may be made of 3S, 4S or 52S alloys.

The writer was interested to learn that the Knolls Laboratory at Schenectady employs a central water de-ionizer with water being piped to all laboratories in brass or copper pipes. The central installation has a capacity of 2,000 gals. per hour using only water produced at or near peak efficiency of the system. With this procedure it is expected to obtain water of low soluble salt content. It was reported that the de-ionizer employed is of a new type that removes silica from the water. Information on the system may be obtained from the Cyanamide Company Sales office in New York City.

If the de-ionizer referred to does completely remove silica, it represents a great step forward in the production of pure water. The writer suggests that tests be made at Knolls to determine the actual quality of the water produced. Silica and total solids would be the particular values of interest.

PERSONNEL

The purpose of the writer's visit to Oak Ridge on January 23, 1949 was to interview a group of technical men who were to be released from the laboratories at Y-12. Only small units of the electromagnetic plant are operating on special problems; this introduces the necessity of curtailing the laboratory staff. Dr. Larson informed the writer, however, that it is his intention to absorb as many of the men as possible at other Oak Ridge sites or other plants of Carbide and Carbon. Progress in this endeavor had been slower than anticipated and none of the men had yet been notified of the reduction of staff. For this reason he asked that I not talk with any of the men. As soon as it is known which men will be available for possible employment at Hanford, Dr. Larson will send to Mr. Mc Lenegan the personnel records of those men and the supervisor's comments regarding the individuals.

The writer had a brief discussion with Dr. Hunt at Schenectady. He explained that the recent delay in our receipt of interview data resulted from the accumulation of large amounts of work during his month's absence from the office. He pointed out that the present system of handling interview data has just been inaugurated and that we can expect more efficient operation in the future.

Dr. Hunt asked that Mr. Mc Lenegan send him a supply of Hanford application blanks (HW 4.38).

During the Pittsburgh Symposium the writer had opportunity to talk with Dr. T. I. Taylor of the Analytical Department of Columbia University. The latter named two men graduating with the Ph. D. degree in June:

Irving Ruderman was indicated to be a very capable man with the ability to direct research problems. He has a wide field of interest and has specialized in the applications of radio technique to radio chemical problems as well as the use of X-ray, spectrographic and microscopy methods. His research is on the subject, "Scattering of neutrons by para-magnetic compounds".

William Spindel is at present a Du Pont fellow working on the problem of isotope separation. He has had experience at Los Alamos on mass spectrometry and vacuum fusion. He was represented to be energetic and to have good laboratory technique.

The writer recommends that both these men be contacted regarding possible Hanford employment.