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LOS ALAMOS DISCUSSIONS - METHODS OF ANALYSIS OF PLUTONIUM METAL

During the period of October 30 - November 1 representatives of the Hanford Works and Los Alamos Laboratories met at Los Alamos for a series of conferences on final metal product specifications. That part of the discussions dealing with the chemical purity specifications, analytical methods employed at the two sites for the determination of impurities and comparison of analytical results currently obtained at the two sites is the subject of this memorandum.

Summary and Conclusions:

1. A Los Alamos program for redetermining the relationship between q values and neutron emission may lead to a revision of chemical specifications. However in any move to change specifications the practical question of what is the purest plutonium that can be produced at a reasonable cost is not likely to be ignored. This cannot be answered until Hanford analyses are put on a firmer basis than at present.

2. There is every reason to believe that the Los Alamos modification of the cupferron method will result in more accurate determinations of plutonium metal impurities than at present. Work is now underway to confirm their results. If confirmation is obtained the new method will be incorporated in Hanford control procedures. It appears probable that the net effect of the new procedure on c/q summations will be generally lower values than hitherto reported at Hanford and a smaller number of pieces reported as out of specifications.

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3. Comparison of the quality of metal produced here and at Los Alamos will be possible after improved methods have been put into use at Hanford and sample exchanges with Los Alamos completed successfully. With demonstrated agreement of methods at the two sites, differences in quality of product can be evaluated.

Background:

Before describing the Los Alamos meetings it is in order first to review the state of knowledge prevailing here prior to the meetings. Inclusion of analytical questions in the agenda of the meetings was catalyzed, primarily, by the fact that in recent months a number of Hanford processes have, according to Hanford analyses, come perilously close to or exceeded the limiting impurity tolerance in respect to α, n reactions. This tolerance is expressed by the equation $\Sigma c_i/q_i \leq 1.00$, where c_i and q_i are for a given element the concentration in p.p.m. and a constant related to the α, n cross-section, respectively. These high summations could be explained on one or all of three bases: (1) the q values might be in error, (2) the analyses might be in error, (3) Hanford might simply be producing a poor quality metal.

In respect to item (1), a value of 1.00 for the secondary quantity, $\Sigma n\, c_i/q_i$, is intended to correspond to a value of 3.0 for the functional quantity, n/g/sec. (due to α, n reactions). Any error in establishing the relationship between the two quantities would presumably require a revision of the q values. Information on this matter was needed from Los Alamos.

Hanford methods of analysis for impurities in plutonium metal have never been regarded as entirely satisfactory, nor were Los Alamos methods until recently. The impurities of importance from a nuclear point of view are boron, fluorine, carbon, magnesium, beryllium, aluminum, sodium, lithium and silicon. The first three elements are determined by non-spectrographic methods both here and at Los Alamos and the methods are believed to be fairly accurate. Silica has always been determined by the same method here and at Los Alamos, and although the accuracy of the determination is subject to some uncertainty the practical effect is slight because of the high q value of silicon. It is the determination of the remaining elements, particularly magnesium, that has been a matter of concern. At the start-up of 234-5 operations the accepted method for determination of these elements was the cupferron-copper spark spectrographic procedure. There was then no reason to doubt the accuracy of the results, but in order to confirm this the carrier concentration method was adapted for determination of plutonium impurities. Higher results than by the cupferron method were obtained and wherever independent checks by the direct copper spark method were possible much closer agreement with the carrier concentration than with the cupferron results were obtained. Later it was rather conclusively shown by development studies that the cupferron method gave results that were poorly reproducible and low by a factor of two to three or more for "q" elements and heavy element impurities. For over a year, therefore carrier concentration results have been reported wherever the method is sufficiently sensitive, i.e., of the "q" element, magnesium and sodium have usually been reported on the basis of this method, whereas aluminum, beryllium and lithium have usually been reported on the basis of the cupferron determination. The net effect has been higher c/q summations reported than would be obtained by maximum dependence on the cupferron method, primarily because of the high contribution of magnesium. The present system, although more realistic than the exclusive use of the cupferron method, has nevertheless probably given high results, there being reason to suspect that carrier concentration results may be high by perhaps a factor of two. Because of this situation, development of a TTA extraction-copper spark method was started early in 1950.

In August of this year, before the TTA work had been completed here, word was received from Dr. C. F. Metz that a program for improving and revising the cupferron procedure was nearing completion in the Los Alamos Laboratories. No working information was made available to us at that time, however. From the analytical point of view, the primary purpose of the Los Alamos conferences was to obtain information about this improved cupferron procedure.

Los Alamos Information:

It was found at Los Alamos that establishment of q values in terms of the functional quantity n/g/sec. (due to α, n reactions) was in no way tainted by use of erroneous analytical data. The q values were established by use of α, n cross-section data; validity of the cross-sections used is questionable, however, since massive targets and alpha particles of different energies than those obtaining in plutonium metal were employed. Los Alamos plans to redetermine the relationship by preparing very pure plutonium metal, adding known amounts of each impurity of nuclear significance to the metal and measuring the increase in neutron count directly.

Inspection of the data obtained by Los Alamos in the development of their new cupferron method leaves very little reason to doubt that analysis of impurities in plutonium has been put on a vastly improved footing. Working details of the new method have been given to Hanford analytical research and development personnel. After equipment and materials have been assembled and familiarity gained in the use of the new method, sample exchanges will be arranged. It will probably not be possible to incorporate all of the improvement features of the Los Alamos method into Hanford control procedures for two or three months; however the most important feature is one that can be adopted sooner.

In highlight, the Los Alamos findings are as follows: By the old cupferron method a Pu^{+3} or Pu^{+4} cupferron complex is extracted from the aqueous phase

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by chloroform and ether. The aqueous phase, containing the impurity elements, is evaporated down, treated with 16 N HNO_3 for destruction of organic material, treated with hydrochloric acid and transferred to the electrodes and subjected to copper spark excitation. The principal source of error in this procedure was found to be incomplete destruction of the organic matter. During sparking the organic matter was prone to "explode" or scatter and excitation was thus incomplete and erratic, leading to low results and poor precision. By the new method complete destruction of organic matter is obtained by following nitric acid treatment with perchloric acid treatment. Other secondary but important features of the new procedure include use of quartz equipment where pyrex was formerly used and use of highly purified cupferron. Both changes reduce contamination by sodium, calcium and magnesium. In the course of the development work it was shown that extraction of impurities into the ether or chloroform is not a significant source of error; the presence of plutonium does not influence the excitation of the impurity elements, thereby simplifying the use of standards; and the old cupferron method was in error by about the same factors found by Hanford. In respect to precision the method appears to be not only better than the old cupferron method but possibly better than the carrier concentration method as well. These conclusions must be tempered by the fact that use of the new cupferron method has been limited to three highly experienced Los Alamos development chemists.

Comparison of impurity analyses on final metal currently produced at Hanford and Los Alamos cannot lead to unambiguous conclusions because difference in both analytical methods and real quality of product are involved. It may be of interest to note, however, that the averages of values recently reported for sodium, aluminum and magnesium were in that order L 10, 18 and 10 at LAMS and 20, 10 and 60 at Hanford Works.

Certain other analytical information of interest was obtained at Los Alamos. It is their experience that use of 4% Ce_2O_3 carrier in the carrier concentration method gives more reliable results than 2%, as used at Hanford and previously used at Los Alamos. Where a choice is possible between the new cupferron method and the carrier concentration method they prefer the former because of greater speed and less radiation hazard. A program is about to be undertaken to define the accuracy of the carrier concentration method. The principal feature of this work will be the preparation of spectroscopically pure plutonium dioxide. A TTA extraction-copper spark method for the determination of impurities in plutonium which has been under investigation at Hanford is also being investigated at Los Alamos. Although their work is incomplete, they do not feel that the TTA method will measure up to the modified cupferron method because of greater difficulty in removing organic material prior to sparking. Working data and procedures were obtained on a new method for the determination of carbon in plutonium. This method is faster and safer than the one now used at Hanford. A comprehensive sampling program will be undertaken at Los Alamos soon to define the extent to which lack of homogeneity of samples causes analytical errors.

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