

which Fischer¹¹ has so thoroughly investigated. Our experience indicates that dithizone is a good deal more sensitive than the hydroxyanthraquinones (thus ϵ_2 for copper dithizonate is about 35,000^{11a}; ϵ_2 for the zirconium-quinalizarin lake is only 10,000); that the former reagent is much more difficult to prepare and to keep unchanged; that procedures involving it are likely to be more tedious, and that precise results are more difficult to obtain when it is used.

Summary

With the aid of a photoelectric recording spectrophotometer, precise colorimetric methods for the determination of zirconium or hafnium in small amounts have been developed. The methods involve lake formation with the hydroxyanthraquinone dyes.

Hafnium and zirconium, while qualitatively indistinguishable, can be estimated in a known weight of sample provided other cations can be removed if they are present.

(11) References to Fischer's valuable work are given by (a) Lieb-hafsky and Winslow, *THIS JOURNAL*, **59**, 1966 (1937), who used the spectrophotometer to study dithizone as a colorimetric reagent.

The effect on lake formation of varying the acid concentration has been studied.

Interference by other cations is negligible unless these are present in larger excess.

The decrease in lake formation caused by complex formation between zirconyl and sulfate ions has been investigated. This decrease is pronounced enough to warrant the belief that the colorimetric methods could be used for the estimation of the various anions, particularly fluoride, that form complexes of this kind.

The scattering of light by the lakes, which are present as suspensions in the alcoholic dye solutions, has been briefly investigated and discussed.

A comparison of the hydroxyanthraquinones with dithizone, another colorimetric reagent that reacts with many cations, shows the latter to be several times more sensitive while the former are simpler to prepare and keep, and are capable of giving accurate results with the expenditure of less time and effort.

SCHENECTADY, N. Y.

RECEIVED JUNE 9, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AND RADIATION LABORATORY, DEPARTMENT OF PHYSICS, UNIVERSITY OF CALIFORNIA]

Artificial Radioactivity as a Test for Minute Traces of Elements

BY G. T. SEABORG AND J. J. LIVINGOOD

The high voltage and large current of the Berkeley cyclotron¹ have made it possible to obtain radioactive isotopes with activities of extremely high intensities, especially when deuterons are used as the bombarding particles. It is the purpose of this note to show how this circumstance has made it possible to identify extremely small amounts of impurities by means of their characteristic half-lives, after the substance containing the impurities has been bombarded with deuterons in the cyclotron. A quantitative estimation of the amount of the impurity can be made in those cases where the yield of the reaction involving the impurity has been previously determined. In the cases where this yield is not known an estimate can be made by means of a comparison with the known yield of some reaction of the same type. As an example the detection of extremely small

amounts of gallium in iron is described. Other examples are given more briefly.

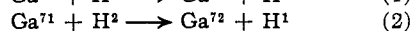
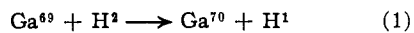
When a sample of iron was bombarded with deuterons it was found that two of the radioactivities produced could be ascribed to an extremely small amount of gallium impurity in the iron (~ six parts in one million, as will be shown later). This was established by the fact that the half-lives of the two activities, 22 min. and 14 hr. (electron emitters), were identical with the known half-lives of electron emitting Ga⁷⁰ and Ga⁷², respectively.^{2,3} A chemical separation according to the methods of Noyes and Bray was performed upon a sample of bombarded iron to which a small amount of "carrier" gallium had been added after the bombardment. The 22 min. and 14 hr. periods appeared only in the gallium fraction.

(2) Amaldi, D'Agostini, Fermi, Pontecorvo, Rasetti and Segre, *Proc. Roy. Soc. (London)*, **A140**, 522 (1935).

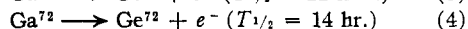
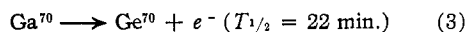
(3) Sagane, *Phys. Rev.*, **53**, 212 (1937).

(1) Lawrence and Livingston, *Phys. Rev.*, **45**, 608 (1934); Lawrence and Cooksey, *ibid.*, **50**, 1131 (1936).

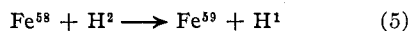
The radioactive isotopes are formed according to the reactions



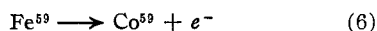
and decay as follows



It would be possible to make an accurate estimate of the amount of gallium impurity in the iron if the cross section of reaction (1) or (2) were known, but the yield of these reactions has not been determined. However, an approximate estimate of the amount can be made by comparing the initial intensity of Ga^{70} or Ga^{72} with the initial intensity of another radioactive isotope formed by the same type of reaction under the same conditions from an isotope of known concentration. It has been established⁴ by chemical separations that one radio-iron isotope is produced when iron is bombarded with deuterons (in addition to several radio-cobalt and radio-manganese isotopes), and that this radio-iron activity is due to Fe^{59} produced according to the reaction



The Fe^{59} emits electrons and decays with a half-life of 47 days

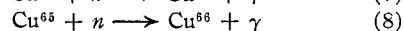
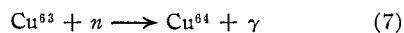


Iron and gallium were separated together by an ether extraction from a sample of iron which had been bombarded in the cyclotron for forty-five minutes with 50 microamperes of deuterons with 6.4 million electron volts of energy. The initial measured activities of the 22 min. Ga^{70} , 14 hr. Ga^{72} and 47 day Fe^{59} , as measured with a Lauritsen type quartz fiber electroscop, were 0.12, 0.0033 and 0.10 divisions/sec., respectively. After correction to infinite bombardment time (through the relation $N_0 = N_\infty (1 - e^{-0.693 t/T_{1/2}})$), these initial activities become 0.16, 0.091 and 217 divisions/sec., and these corrected initial activities should be proportional to the concentrations of Ga^{69} , Ga^{71} and Fe^{58} in the bombarded iron. (This assumes that the cross sections of reactions (1), (2) and (5) are equal; they should be nearly equal for elements of nearly the same atomic weight.) It is known that the concentration of Fe^{58} in iron⁵ is 0.5% and that gallium⁵ is composed of 61.2% Ga^{69} and 38.8% Ga^{71} . Therefore the corrected initial intensities of Fe^{59} and either Ga^{70}

or Ga^{72} , together with these abundance ratios, lead to a concentration of six parts per million of gallium in the bombarded iron. One-tenth this much could readily have been detected.

The half-life of an activity can be established quite well (unless it is very short) if it has an initial measured intensity of several times the background (natural leak) of the electroscop. Radioactive isotopes with initial measured activities of ten million times the electroscop background can be formed in many elements (*e. g.*, manganese, nickel, copper) by deuteron bombardments of the order of 100 microampere-hours at 6 to 8 million electron volts. Thus when these elements are present as impurities to as small an extent as one part in a million they can be detected after a deuteron bombardment has been made. The radioactive atoms formed from such minute impurities often must be chemically separated (after the addition of inactive material to act as "carrier") in order that their weak activities may not be buried in the much stronger radiation of the main activity.

On the other hand, larger amounts of impurities (0.01–0.1%) often can be detected by measuring the composite decay curve of a bombarded sample which has not been subjected to a chemical separation. Upon the analysis of the decay curve extraneous periods appear which can be attributed to known radioactive isotopes and hence can be used to identify some of the impurities in the bombarded sample. This method has the advantage that the material is not used up or disturbed in any way. In this manner the presence of a small amount of copper in nickel was established as the result of a neutron bombardment of the nickel. (The neutrons were produced by the reaction of deuterons with beryllium.) The well-known 6 min. electron emitting activity² of Cu^{66} and the 12.5 hr. positron and electron emitting activity⁶ of Cu^{64} appeared. These were formed according to the reactions



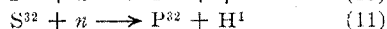
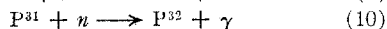
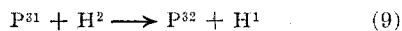
The presence of a small amount of iron in a sample of cobalt oxide was established by a deuteron bombardment of the oxide. The analysis of the composite decay curve revealed an 18-hr. positron emitting activity. It has been shown that this activity is due to a radio-cobalt which can be formed only by the bombardment of iron.⁴

(4) Livingood, Seaborg and Fairbrother, *Phys. Rev.*, **62**, 135 (1937).

(5) Livingston and Bethe, *Rev. Modern Phys.*, **9**, 380 (1937).

(6) Van Voorhis, *Phys. Rev.*, **49**, 876 (1936).

In other experiments it has been possible to establish the presence of extremely small amounts of phosphorus and sulfur as a result of the appearance of the 14-day electron emitting activity of P^{32} . The P^{32} was formed according to the reactions



For example, a neutron bombardment of a sheet of paper revealed the presence of the sulfur as the result of reaction (11).

This research has been made possible through the generous cooperation of the Research Corporation, the Chemical Foundation and the Josiah Macy, Jr., Foundation.

Summary

It is shown how it is possible to detect and identify very small amounts of impurities by means of their characteristic half-lives, after the substance containing the impurities has been rendered radioactive by bombardment with charged particles of high energy or with neutrons. With the help of a chemical separation after the bombardment, impurities present to the order of one part in a million can sometimes be detected. For example, a gallium impurity of six parts per million was found in a sample of iron. Impurities to the extent of one part in one thousand to ten thousand can often be detected without subjecting the sample to chemical analysis.

BERKELEY, CALIFORNIA

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 642]

The Magnetic Properties and Structure of Manganous and Cobaltous Dipyrindine Chlorides

BY DAVID P. MELLOR AND CHARLES D. CORYELL

It has been reported by Cox, Shorter, Wardlaw, and Way¹ on the basis of a determination of unit cell dimensions that manganous dipyrindine chloride and the α -form of cobaltous dipyrindine chloride have square *trans*-coördination of pyridine and chlorine about the metal atoms. Complexes of atoms with square bonds have been the object of much interest since this type of structure was first proposed by Werner to explain the existence of certain isomeric platinum compounds.² With the extension of our knowledge about the nature of chemical bonds there has been formulated³ a reliable magnetic criterion by which the existence of square covalent structures for manganous, ferric, ferrous, cobaltic, cobaltous, and nickelous atoms may be determined. It is concluded in this paper that the results of magnetic measurements on the manganous and α -cobaltous dipyrindine chlorides are not compatible with the square coördinated structure proposed by Cox and co-workers, but that they are compatible with an octahedral ionic type of structure.

Magnetic measurements were carried out on the manganese compound by the Gouy method.

(1) E. G. Cox, A. J. Shorter, W. Wardlaw, and W. J. R. Way, *J. Chem. Soc.*, 1556 (1937).

(2) A. Werner, *Z. anorg. allgem. Chem.*, **3**, 267 (1893).

(3) L. Pauling, *THIS JOURNAL*, **53**, 1367 (1931).

The forces in mg. (Δw corrected for blank) for a cylindrical tube with water in the upper compartment and air in the lower compartment were for two different field strengths -2.03 and -3.39 . The forces with manganous dipyrindine chloride, twice crystallized from ethanol and packed to a density of 0.99, g./ml., were $+135$ and $+234$, respectively, at 22° against air. With use of an estimated value of -160×10^{-6} for the molecular diamagnetism of the compound and with the assumption of the validity of Curie's law, the calculated values of the magnetic moment are 5.94 and 6.00 Bohr magnetons, the average being 5.97. The expected value of the moment for the manganous atom forming four dsp^2 bonds, essentially covalent and directed toward the corners of a square, is 3.88 plus a small orbital contribution; the expected value for the atom with tetrahedral sp^3 bonds or for the ion is 5.92 magnetons with no orbital contribution (normal state $^6S_{5/2}$). The measurements are in good agreement with the second of these values.

Barkworth and Sugden⁴ have shown that the α -form (violet modification) of cobaltous dipyrindine chloride has a moment of 5.34 Bohr magnetons, and that the β -form (blue modification) has

(4) E. D. P. Barkworth and S. Sugden, *Nature*, **139**, 374 (1937).