A side-reaction, *i. e.*, the discharge of hydroxyl ions, leads to liberation of oxygen

$$2OH^- + 2\oplus \longrightarrow H_2O + O$$

The electrolysis results in aqueous ammonia being formed at the cathode, iodine with nitrogen and oxygen gas at the anode.

ROUDNICE, CZECHOSLOVAKIA
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[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY]

The Absorption Spectrum of Element 61, Promethium[1,2]

BY G. W. PARKER AND P. M. LANTZ

Introduction

Since the isolation of milligrams[3] of promethium in chemically pure state is now almost routinely performed in this Laboratory, advantage has been taken of the opportunity to investigate some of the properties of the synthetic element. Among the investigations conducted was a study of the absorption of light in the visible spectrum as ordinarily done with the rare earth elements by means of the quartz spectrophotometer.

In the fission products of uranium resulting in the chain reacting pile the 4 year isotope 147 of promethium has been shown to occur with a yield of about 2.5%.[4] Sources of mixed fission products sufficient to yield milligrams of promethium have been isolated and the rare earth elements individually separated by ion-exchange methods to produce the first recognizable quantities of the substance of atomic number 61. While the 4 year half-life of the isotope is sufficient to permit freedom in time for handling and experimentation, in order to make investigations involving milligrams of mass it was necessary to work with curies of radioactivity.

J. A. Marinsky and L. E. Glendenin reported in 1945 the isolation and radiochemical identification of the synthetic rare earth promethium in the uranium fission products. Later Winsberg[5] estimated its half-life through observed decay to be 3.7 years, which would indicate its specific activity to be approximately 0.66 curie per milligram.

Improvements in separation techniques having made available milligram quantities of this element, determination of its specific activity (approximately 0.6 curie per milligram) by weighing and absolute beta counting was performed during the course of this absorption study.

Experimental Details

Material.—Prior to this absorption study, the same sample in the form of $PmCl_3$ was used by L. E. Burkhart, W. F. Peed and E. J. Spitzer[6] (Oak Ridge Electromagnetic Plant) to record the K and L emission lines of the X-ray spectrum of promethium. About 3 mg. of the sample of promethium was recovered from the X-ray tube and was tested for purity[7] before spectrophotometric study was made, by comparing copper spark spectrograms with the known lines of the other rare earths and those characterized at this laboratory for promethium.[8] Part of this sample was used by C. Feldman[9] (this Laboratory) to look for "Illinium" lines reported by Harris, Hopkins and Yntema.[10] The results of the spectrographic purity test are given in the table below:

TABLE I

IMPURITIES FOUND IN PROMETHIUM (20–30 MICROGRAMS)

Analyzed by the copper spark method on a Jarrell-Ash grating spectrograph

		Elements not found
Al	Trace	Ag, As, Au, B, Be, Bi, Cd,
Ca	Strong	Ce, Co, Dy, Er, Eu, Ga, Gd,
Cr	Moderate	Ho, K, La, Li, Lu, Mn, Mo,
Fe	Faint trace	Nd, Ni, Pr, Rb, Sb, Si, Sm,
Mg	Moderate	Sn, Sr, Ta, Ti, Tm, V, Zn
Na	Trace	
Pb	Very weak	
Pt	Presence questionable	

In preparation for absorption study, the portion of the sample remaining after applying the spectrographic test above was analyzed for gross beta activity by absolute beta counting techniques and was found to be 822 mc. It was then converted to the $PmCl_3$ and was transferred in 0.2 ml. of 0.1 *N* HCl solution to a calibrated semi-micro quartz cell 2.5 mm. × 10 mm. (10 mm. length of light-path).

After the study was completed the promethium was converted to the oxalate and weighed. Then the oxalate was ignited to the oxide and reweighed.

The promethium (calculated as 0.926 mg. of the element) obtained as the oxide was then found to be 551 mc. On the basis of this weight-activity relationship the mo-

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[1] This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

[2] The name promethium is used in view of the action of the International Union of Chemistry at the XVth Conference at Amsterdam, September, 1949, reported in the *Chemical and Engineering News*, **27**, 2996 (1949). The declassified manuscript on which this paper was based was one of the important ones used in establishing the validity of the promethium claim.

[3] G. W. Parker and P. M. Lantz, Oak Ridge National Laboratory Report, ORNL-75, "The Separation of Milligram Quantities of Element 61 from Fission," June, 1948; AECD-2160, May 27, 1949.

[4] J. A. Marinsky, L. E. Glendenin and C. D. Coryell, THIS JOURNAL, **69**, 2781 (1947).

[5] J. A. Seiler and L. Winsberg, Paper 190, Vol. 9, Div. IV, National Nuclear Energy Series, McGraw-Hill, 1950.

[6] L. E. Burkhart, W. F. Peed and E. J. Spitzer, "The K Spectra of Element 61," *Phys. Rev.*, **75**, 86 (1949); "The L Spectra of Element 61," *ibid.*, **76**, 143–144 (1949).

[7] Private communication from M. Murray, Oak Ridge National Laboratory, April, 1949.

[8] D. Timma, "The Spark Spectra of Elements 43 and 61," *Journal of the Optical Society of America*, **39**, 898–902 (1949).

[9] C. Feldman, "Note on the Arc Spectrum of Element 61," THIS JOURNAL, **71**, 3841–3842 (1949).

[10] J. A. Harris and B. S. Hopkins, *ibid.*, **48**, 1585 (1926); L. F. Yntema, *ibid.*, **48**, 1598 (1926).

larity (0.0472) of the solution employed in the absorption band study of the chloride was calculated.

Apparatus.—For this investigation a Beckman Spectrophotometer Model LD was employed using a special RCA C7032 photo-tube for measurements below 625 millimicrons and an RCA Type 919 cesium oxide photo-tube for measurements above 625 millimicrons. A defining slot 1 × 2 mm., punched from a piece of 0.004 in. steel shim stock, was inserted on the light source side of the cell, being held in place with tape. The defining slot was necessary to diminish the standard 3 × 6 mm. light beam so that it would fall within the limits of the small cross section of the solution exposed. Before securing the defining slot it was so aligned that the light emanating from it would pass directly through the liquid column in the positioned quartz cell, without interference from the sides of the cell.

Wave length calibration of the Beckman Spectrophotometer was done with both mercury and hydrogen arc lamps, after the instrument had been adjusted for focus of maximum light. For two of the mercury emission lines, 253.6 and 546.0 mμ, and also for one of the strongest hydrogen lines, 656.27 mμ, agreement within 0.5 mμ was obtained, while for the 1014 mμ mercury line the best instrument value was 1020 mμ. This agreement in calibration seemed to be satisfactory since the most prominent absorption bands in the visible spectrum for promethium appear in the region from 400 to 790 mμ.

Procedure.—After the $PmCl_3$ solution was transferred to the quartz cell and the blank prepared, the cells were sealed with tape to prevent evaporation in order to insure maintenance of a constant concentration throughout the period of measurement. Transmission readings on the Beckman Quartz Spectrophotometer were taken from 350–1000 mμ at 5 mμ intervals except when a change in absorption was indicated, at which time readings at 1 mμ intervals were taken to determine accurately the wave length at which maximum absorption was obtained.

In order to provide data on the concentration of the material used in this absorption study it was put through another purification, preparatory to weighing, by means of several reprecipitations as the oxalate and hydroxide. This repurification was considered necessary because of the contamination contributed by atmospheric dust during the transfer of solutions. Finally the oxalate was transferred to a Gooch-type 2 ml. platinum crucible in which it was weighed on the basis of an assumed formula as Pm_2O_3 following the ignition of the oxalate in an oxygen atmosphere at 650°. The weights obtained for promethium present, weighing as $Pm_2(C_2O_4)_3 \cdot 10H_2O$ and as Pm_2O_3, checked within 0.3%.

Absorption studies have been made of approximately twelve different promethium preparations of various concentrations of chloride and nitrate solutions on the same calibrated spectrophotometer with remarkably good agreement. For the sake of further comparison several samples of spectrographically pure neodymium nitrate of known concentration were examined on the same instrument, and the absorption bands obtained compared favorably with those published by Rodden.[11] In order to show more clearly the weak, as well as the more prominent absorption bands, a molar extinction coefficient plot was made in the manner according to Brode,[12] Fig. 1. For a comparison of the bands of absorption of $Nd(NO_3)_3$ and $Pm(NO_3)_3$ relative to their position and intensities, reference is made to Fig. 2.

Experimental Results

Absorption data obtained in studies of both the $PmCl_3$ and $Pm(NO_3)_3$ seem to indicate that they possess the same absorption characteristics in solution, Fig. 2.

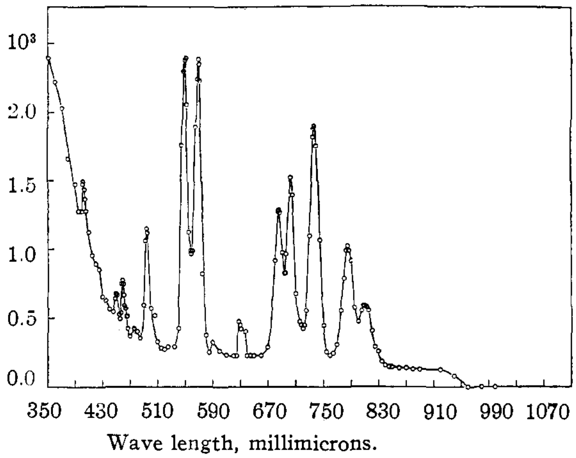

Fig. 1.—Molecular extinction of $PmCl_3$ 0.0472, molar solution, 10 mm. cell length.

It is interesting to note in Fig. 2 that the major bands of absorption of promethium are approximately the same in number and have the same general location in the visible spectrum as those of its rare earth neighbor, neodymium. However, by referring to Fig. 2, it is evident that the closest any prominent bands for neodymium approach those of promethium is of the order of 8 mμ which is considerably outside the limits of experimental error. The maximum deviation observed in the location of the ten major absorption bands was less than 1.0 mμ.

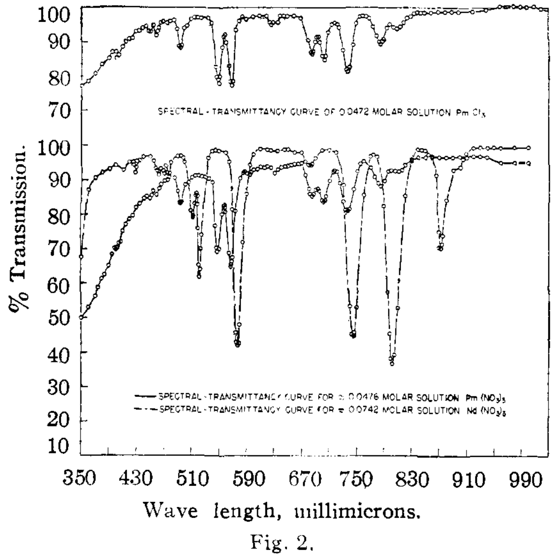

Fig. 2.

Table II, below, summarizes the positions and relative intensities of the ten major bands observed. Bands 548.5 ± 0.5 mμ, 568.2 ± 0.2 mμ, and 737.2 ± 0.2 mμ due to their greater intensity could conceivably be used for the purpose of identification of very low concentrations of promethium solutions.

No investigation was made to determine whether the molar extinction coefficients changed with concentration.

The very weak band appearing at 402.5 ± 0.5 mμ is assumed to be contributed by the stable samarium isotope 147 resulting from beta decay of 4.0 yr. promethium. This particular spectral band is reported by Yntema[13] as being the most prominent of the samarium bands. The

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[11] C. J. Rodden, *J. Nat. Bur. Stds.*, **26**, Research Paper 1395, June, 1941.

[12] W. R. Brode, "Chemical Spectroscopy," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1943.

[13] L. F. Yntema, THIS JOURNAL, **48**, 1598 (1926).

TABLE II

PRINCIPAL ABSORPTION BANDS OF PROMETHIUM

Wave length, mμ	Molar extinction coefficient, $\epsilon \times 10^{3}$
459.5 ± 0.5	0.7
493 ± 0.5	1.2
548 ± 0.5	2.3
629.0 ± 1.0	0.5
568 ± 0.2	2.3
685 ± 0.2	1.3
702.7 ± 0.2	1.6
737.2 ± 0.2	1.9
785.0 ± 0.2	1.1
810.0 ± 0.1	0.6

remaining spectral bands of samarium, however, do not appear in concentrations of promethium which are three to four times as high as is illustrated in Fig. 2. Due to the fact that measurement of absorption in solution does not distinguish between two adjacent absorption bands separated by only a few ångströms, comparisons with the absorption by the crystals will be undertaken soon. It is hoped that this would also establish whether this weak band at 402.5 ± 0.5 mμ belongs to samarium or to promethium.

It was observed that the crystalline salts, chloride and nitrate, of promethium displayed different colorings. This introduced the question of whether if in solution these salts would have the same optical absorption characteristics; however, when this test was made, it was noted that the coloring of the solutions were visibly the same, *i. e.*, pink or rose. This fact was later indicated by the failure to find any apparent difference in the two spectra.

Other chemical forms of promethium, such as the hydroxide, oxalate and oxide all appear pink or rose.

It was of interest to compare the results of this study of the synthetic element with those reported in 1926 on natural material by B. S. Hopkins, *et al.*[10] Harris and Hopkins concluded that the most probable bands were in the positions 581.6 mμ and 512.3 mμ. A description of the methods used by Hopkins, *et al.*, in studying absorption is not given in the papers cited. The absorption data presented here were obtained with the element in solution and in that form the presence of these lines is not indicated.

Summary

1. The absorption bands of promethium in the visible spectrum are observed to resemble those of neodymium, both in number and in intensity but are distinctly separable from the neodymium bands by at least 8 mμ.

2. The absorption bands of promethium are in the same position and of the same magnitude for both the chloride and nitrate solutions.

3. The most prominent absorption bands for a solution of promethium are to be found in positions 493.5 ± 0.5 mμ, 548.5 ± 0.5 mμ, 568.0 ± 0.2 mμ, 685.0 ± 0.1 mμ, 702.7 ± 0.3 mμ, 737.2 ± 0.2 mμ, and 785.0 ± 0.1 mμ.

OAK RIDGE, TENN.

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Absorption Spectroscopic Studies of Hydrogen Bonding and Isomeric Forms in Bis-phenol Alkanes

BY NORMAN D. COGGESHALL

The present report is of infrared and ultraviolet absorption spectroscopic investigations made on a series of bis-phenol alkanes. These compounds are formed by the bridging of two phenolic nuclei through an aliphatic group which may be of various forms. Such materials have been referred to elsewhere as dihydroxyphenols or in some cases as diphenylolmethanes.[1] During some molecular structure determination work it was discovered that the bis-phenol alkanes had unusual hydrogen bonding characteristics. It was found that some members of the species may exist in three states, with regard to the hydrogen bonding. Some molecules may be intermolecularly bonded, some may be in a *cis*-isomeric form and some may be in a *trans*-isomeric form. The *cis*- and *trans*-isomeric forms, as used here, are not true isomeric forms but refer to orientation configurations. The *cis* form is that orientation wherein the two hydroxyl groups on the two phenolic nuclei are close together and hydrogen bonded to each other. The *cis* form hence exhibits intramolecular hydrogen bonding. The *trans* form is that orientation wherein the two hydroxyl groups are sufficiently removed from each other that no hydrogen bond exists and yet the hydroxyls are not members of intermolecular bonds. The fact that a *trans* form can exist in concentrated solutions of some of the phenols is due to the steric hindrance offered by ortho substituted *t*-butyl groups. The steric hindrance to intermolecular bonding offered by large ortho substituted alkyl groups in the mono-nuclear phenols has been previously discussed[2,3] and some of the results are applied here.

Experimental Details

Infrared Absorption.—The infrared absorption data were obtained with an automatic recording Perkin–Elmer Model 12B infrared spectrometer. A LiF prism which gives excellent dispersion in the 2.6–3.0 μ region was used. The quantitative data were obtained with a cell-in-cell-out arrangement previously described.[4]

Each compound was examined under four different conditions. As received, the materials were generally a powder of small crystals which had not at any time been exposed to melting temperatures. Since melting sometimes changes the distribution among the various states the materials

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[1] H. L. Bender and A. G. Farnham, U. S. Patent 2,464,207.

[2] N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947).

[3] N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

[4] E. L. Saier and N. D. Coggeshall, *Anal. Chem.*, **20**, 812 (1948).