

## Benzoyl-*m*-nitroacetanilide as a Gravimetric Reagent for Beryllium

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Small quantities of beryllium (2.0 to 3.0 mg) have been determined gravimetrically with benzoyl-*m*-nitroacetanilide. The yellow complex is precipitated from solutions of pH 6.5 to 9.0 and weighed directly as  $\text{Be}(\text{C}_{15}\text{H}_{11}\text{O}_4\text{N}_2)_2$  containing 1.58% of the metal after drying at 120° or after ignition to oxide. Using thioglycolic acid, magnesium-EDTA and/or  $\text{H}_2\text{O}_2$  as masking agents separation from  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Th}^{4+}$ ,  $\text{TiO}^{2+}$ ,  $\text{VO}^{2+}$  and  $\text{UO}_2^{2+}$ , have been effected. The relative standard deviation is only 0.27%. The method is also applicable to the determination of beryllium content of beryl.

Until 1961, no organic precipitant had been reported to form any complex with beryllium that could be weighed directly. Several reagents<sup>1-6</sup> are now known which have been used successfully for the gravimetric determination of this metal. However, it is felt that still there is some scope for finding a better reagent which will give a complex having lower solubility in hot water or alcohol as well as of better thermal stability. Benzoylacetanilide<sup>6</sup> has been found to be a good reagent for beryllium, but the precipitate is formed only slowly and it has some solubility in hot water (above 70°) specially when some alcohol is present (above 30% by volume). The introduction of a nitro-group in benzoylacetanilide has been found to cause a vast improvement in its quality as a reagent.

In the present investigation benzoyl-*m*-nitroacetanilide has been found to precipitate beryllium almost instantaneously in an easily filtrable form, which is insoluble for all practical purposes up to 95°, even in the presence of considerable amounts of alcohol. Separation from most of the metal ions commonly associated with beryllium, was possible using suitable masking agents like magnesium ethylenediamine tetraacetate (Mg-EDTA) or thioglycolic acid. The precision and accuracy of the method were very satisfactory, the standard deviation being 0.27% in 32 determinations. By masking the foreign ions with Mg-EDTA, beryllium content of beryl could also be determined with high accuracy.

### EXPERIMENTAL

*Benzoyl-m-nitroacetanilide*: The reagent was prepared in the laboratory following the method due to Weisberger<sup>7</sup> *et al.* An ethanolic solution of the reagent was used.

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*Beryllium solution* : Beryllium hydroxide was precipitated from a solution of beryllium nitrate (E. Merck) in the presence of disodium-EDTA, washed with water, dissolved in nitric acid and diluted. The metal content of the solution was determined gravimetrically.

*Diverse ions* : Aqueous solutions of other metal ions were prepared from sulphates, chlorides or nitrates. Little quantities of an acid were added to avoid hydrolysis where necessary.

*Mg-EDTA solution* : Solutions of EDTA (Titriplex III, E. Merck) (1M) and magnesium chloride (1M) were prepared separately; 2 ml portions of each were mixed before use.

All the reagents were of A.R. or G.R. grade.

*Apparatus* : A battery operated bench model Cambridge pH-meter was used.

*Procedure* : About 2.0 to 3.0 g of ammonium chloride was added to a known quantity of the stock beryllium solution, diluted to 150 ml and heated almost to boiling. Benzoyl-*m*-nitroacetanilide solution (0.18 to 0.20 g in 15 ml ethanol) was added dropwise with constant stirring and the pH was adjusted between 6.5 and 9.0 with aqueous ammonia (2N). A yellowish precipitate was immediately formed, which was digested for about half an hour on a hot water-bath with occasional stirring before filtration. The precipitate was then washed with hot water (80°), ignited to oxide and weighed.

In another set of experiments, the beryllium complex was filtered on a weighed sintered glass crucible, washed as before and weighed after drying at 120°. Beryllium content was calculated on the basis that the precipitate contained 1.567% of the metal. The results of these determinations are given in Table I.

TABLE I

*Determination of Beryllium*

Be taken, mg	Weighed as BeO		Weighed as Be(C <sub>15</sub> H <sub>11</sub> O <sub>4</sub> N <sub>2</sub> ) <sub>2</sub>		
	Be found, mg	Rel. Error, %	Wt. of complex, g.	Be found, mg	Rel. Error, %
2.05	2.05	nil	0.1313	2.06	+0.48
	2.06	+0.48	0.1310	2.06	+0.48
2.58	2.59	+0.38	0.1647	2.58	nil
	2.59	+0.38	0.1651	2.59	+0.38
2.86	2.85	-0.35	0.1825	2.86	nil
	2.86	nil	0.1822	2.86	nil

*Procedure in the presence of diverse ions* : The procedure described above could be applied when cobalt (II), copper (II), lead (II), nickel (II), zinc (II), aluminium (III), iron (III), chromium (III), cerium (IV), thorium (IV) or vanadium (IV) was present in

appreciable amounts compared to beryllium, provided the foreign ions were masked by the addition of 4 ml of Mg-EDTA before the addition of the reagent. For separating beryllium from titanium (IV), 2 to 3.0 ml of hydrogen peroxide (30 vol.) were required in addition to 4.0 ml of Mg-EDTA solution to mask the latter ions. Thioglycolic acid (1 ml.) was used to mask manganese (II) or uranium (VI) while precipitating beryllium in presence of these ions.

In all these separation procedures the *pH* of the solutions were adjusted between 7.0 and 7.5 with the addition of aqueous ammonia. The results of the separations are presented in Table II.

TABLE II  
*Separation of Beryllium from Diverse Ions (pH 7.0-7.5)*

Be taken, mg	Diverse ion added, mg	Masking agent	Wt. of complex, g.	Be found, mg	Rel. Error, %
2.58	Co <sup>2+</sup> , 25	(a)	0.1644	2.58	nil
			0.1646	2.58	nil
2.86	Cu <sup>2+</sup> , 25	(a)	0.1827	2.87	+0.35
			0.1834	2.87	+0.35
2.86	Mn <sup>2+</sup> , 25	(b)	0.1835	2.87	+0.35
			0.1824	2.86	nil
2.86	Pb <sup>2+</sup> , 25	(a)	0.1833	2.87	+0.35
			0.1835	2.87	+0.35
2.58	Ni <sup>2+</sup> , 25	(a)	0.1646	2.58	nil
			0.1645	2.58	nil
2.58	Zn <sup>2+</sup> , 25	(a)	0.1642	2.57	-0.38
			0.1640	2.57	-0.38
2.58	Al <sup>3+</sup> , 25	(a)	0.1647	2.58	nil
			0.1651	2.59	+0.38
2.86	Cr <sup>3+</sup> , 25	(a)	0.1825	2.86	nil
			0.1818	2.85	-0.35
2.58	Fe <sup>3+</sup> , 25	(a)	0.1645	2.58	nil
			0.1642	2.57	-0.38
2.86	Ce <sup>4+</sup> , 25	(a)	0.1835	2.87	+0.35
			0.1826	2.86	nil
2.86	Th <sup>4+</sup> , 25	(a)	0.1820	2.85	-0.35
			0.1825	2.86	nil
2.86	TiO <sup>2+</sup> , 25	(a)-(c)	0.1822	2.86	nil
			0.1820	2.85	-0.35
2.58	VO <sup>2+</sup> , 25	(a)	0.1650	2.58	nil
			0.1651	2.59	+0.38
2.86	UO <sub>2</sub> <sup>2+</sup> , 25	(b)	0.1832	2.87	+0.35
			0.1835	2.87	+0.35

(a) Mg-EDTA  
(b) Thioglycolic acid  
(c) H<sub>2</sub>O<sub>2</sub>.

*Procedure for Beryl*: A known amount of the mineral (30 to 50 mg.) was fused with 2.0 to 3.0 g of sodium carbonate in a platinum crucible and kept in molten state for about 15 mins. The mass was taken up with hot water, boiled and filtered. The residue left was treated with sufficient amount of hydrochloric acid and 3.0 to 4.0 ml of perchloric acid were added. The mixture was digested for some time and finally evaporated. The mass left was treated with 3.4 *N* hydrochloric acid and filtered. The filtrate was added to the original solution. The insoluble part (chiefly silica) was treated with hydrofluoric acid and sulphuric acid. If any residue was still remaining was fused with potassium bisulphate and mixed with the original solution.

Beryllium content of this solution was then determined with benzoyl-*m*-nitroacetanilide using Mg-EDTA solution as masking agent. The results of these determinations are in Table III.

TABLE III

*Determination of Beryllium in Beryl*

Sample	Weight of ore taken	BeO found by standard method	BeO found by given method
Beryl No. 1	47.2 mg	12.69%	12.62%
	46.8 mg		12.64%
Beryl No. 2	48.1 mg	12.56%	12.48%
	47.5 mg		12.50%

## RESULTS AND DISCUSSION

*Properties and composition of the complex*: The yellow coloured complex was found to be stable up to 290° and appreciably soluble in benzene and chloroform, though practically insoluble in aqueous ethanol.

The pure complex was analysed for the metal content by igniting a known weight of it to oxide and for nitrogen by Duma's method. The experimental results—Be, 1.58% (theo. 1.57%) and N, 9.80% (theo. 9.74%) indicated the formula of the complex to be Be(C<sub>15</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>. Hence beryllium could be precipitated and weighed directly as Be(C<sub>15</sub>H<sub>11</sub>O<sub>4</sub>N<sub>2</sub>)<sub>2</sub>, the factor for beryllium being 0.0158.

*Effect of the concentration of the reagent*: Precipitation of beryllium was carried out at pH 7.0 using different amounts of benzoyl-*m*-nitroacetanilide, the other conditions remaining the same. It was observed that the supernatant liquid after the precipitation of beryllium should be at least 0.02% with respect to the reagent for the quantitative determination of the metal. In cases of all other reagents reported so far for the direct gravimetric estimation of beryllium much larger excess of the reagents are required.

*Effect of pH*: Experimental studies on the precipitation of beryllium from solutions of different pH values, maintaining all the other factors identical, showed that the precipitation commenced at pH 3.0 and the range of complete precipitation was 6.5 to 9.0.

*Effect of sequestering agents* : The precipitation was incomplete in the presence of disodium-EDTA, phosphoric acid, oxalic acid, nitrilotriacetic acid and large amounts of tartaric acid and fluoride. However, in the presence of Mg-EDTA, thioglycolic acid, tri-ethanolamine, hydrogen peroxide and 0.5 g of tartaric acid the estimation was possible. Hence the latter substances could be used for masking the foreign ions to separate beryllium from such ions.

*Precision and Accuracy* : Even though the method was applied to very low quantities of beryllium (2.0 to 3.0 mg in 150 ml) the relative standard deviation was found to be only 0.27% in 32 determinations.

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