USE OF *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE IN ANALYTICAL CHEMISTRY

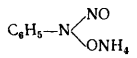
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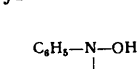
I. INTRODUCTION

Among the nitrogen-containing organic reagents which are greatly used in modern methods of analysis are not only 8-hydroxyquinoline but also the ammonium salt of *N*-nitroso-*N*-phenylhydroxylamine, cupferron [1-3]



the use of which as an analytical reagent was suggested by Baudisch in 1909.[4] However, cupferron has several disadvantages for this purpose. It is unstable to light and heat, and is readily oxidised in the air; the precipitation of cupferron derivatives from hot solutions is accompanied by decomposition and hydrolysis of the reagent. Cupferron derivatives of elements cannot be weighed for gravimetric determinations, but must be ignited to the oxides.

New reagents have therefore been sought which are similar to cupferron in their analytical behaviour but differ from it in not possessing these defects. In 1950 Shome[5] suggested using an analogue of cupferron, *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) for the determination and separation of several elements for which the use of the former is not very convenient. In this compound the nitroso-group has been replaced by benzoyl



BPHA, while closely resembling cupferron in its analytical properties, differs considerably from the latter in other respects, especially in its stability towards light and heat. Several metals form with it crystalline precipitates of definite and constant composition, which may be weighed for gravimetric purposes. The compounds formed by BPHA with metals can in several cases be extracted with organic solvents.

During the past 5-6 years BPHA has attracted the attention of many analysts. The present review, covering the literature up to 1961 (and also the early papers in 1961), discusses the characteristics and the principal analytical applications of BPHA.

II. PREPARATION AND SOME PROPERTIES OF *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE

BPHA was first obtained by Bamberger[6], and Shome[5] only slightly modified the method to prepare the compound for analytical purposes. Phenylhydroxylamine (30 g) is dissolved in 1200 ml warm water, and the solution is filtered; after cooling, a little sodium hydrogen carbonate is added to the filtrate, and 45 g benzoyl chloride is run in with vigorous stirring, about 30 g sodium hydrogen carbonate are added in small portions periodically during this process in order to keep the solution alkaline. After stirring for 90 min, the solid (consisting of a mixture of mono- and di-benzoylphenylhydroxylamine) is filtered off, washed with water, ground in a porcelain mortar with 10% sodium hydrogen carbonate solution, filtered off, and washed with water. This treatment removes occluded benzoyl chloride. Monobenzoylphenylhydroxylamine is separated from dibenzoylphenylhydroxylamine by treatment with aqueous ammonia (sp.gr. 0.88), in which only the monobenzoyl derivative dissolves.

The solution is filtered, and a slight excess of dilute sulphuric acid, cooled in a mixture of ice and salt, is added. The resulting precipitate of monobenzoylphenylhydroxylamine is filtered off, and purified by recrystallisation from alcohol. The final product may also be recrystallised from hot water[7], benzene[8], or concentrated acetic acid (by dilution with water)[9].

Ryan and Lutwick[7] suggested using 3 *N* HCl instead of dilute sulphuric acid to neutralise the ammonia: this avoids the possibility of contamination by the brown oil formed by the oxidation of organic substances when sulphuric acid is used.

Pure BPHA consists of colourless needle-shaped crystals melting at 121°-122°. It is almost insoluble in cold water, but dissolves in hot water, ethyl alcohol, acetone, isopentyl alcohol, chloroform, benzene, cyclohexanone, and many other organic solvents. According to Dyrssen[8] the solubility of BPHA in water at 25° ± 0.3° is 0.00195 M, in good agreement with the earlier value[7,10] of 0.40 g litre^{-1} (0.0019 M). Its solubility in hot water[7] is ~0.5 g in 100 ml. Tables 1 and 2 give the solubility of BPHA in aqueous alcoholic mixtures and in various organic solvents.

Tsê Yün-hsiang[12] worked out a new extraction and spectrophotometric method for determining BPHA in water or in organic solvents, based on its reaction with quinquevalent vanadium. The solubility of BPHA in water at room temperature (~20°), determined by this method, was 0.34 g litre^{-1} (0.0026 M).

BPHA is stable towards air, light, and heat: no decomposition was observed when it was stored dry in an ordinary jar even for three years[12]. It is stable for a long time in

TABLE 1. Solubility of BPHA in aqueous alcohol mixtures at 22° ± 1°.[11]

Ethanol, vol. %	10	20	30	40	50	60	70	80	90	96
Solubility of BPHA, g litre^{-1}	0.610	0.920	1.394	2.732	6.430	11.320	16.625	33.90	87.865	109

TABLE 2. Solubility of BPHA in organic solvents at 22° ± 1°.[11]

Solvent	Solubility of BPHA, M	Solvent	Solubility of BPHA, M
CCl_4	0.026	Benzene	0.150
Xylene	0.034	Ethyl acetate	0.480
Toluene	0.061	Dichloroethane	0.280
Diethyl ether	0.135	Chloroform	0.580

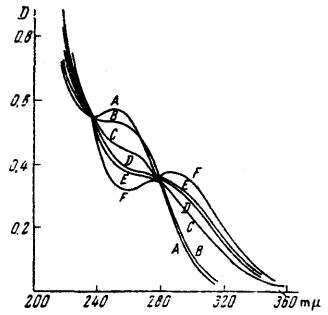


Fig. 1. Absorption spectra of aqueous solutions of BPHA at various pH values: *A*) 0.72–6.43; *B*) 6.8; *C*) 8.37; *D*) 7.85; *E*) 8.06; *F*) 11.20–11.50.

dilute sulphuric and hydrochloric acids (~8 *N*), but it gradually decomposes in dilute nitric acid (>5 *N*); comparatively rapid decomposition is observed also in alkaline and ammoniacal media[9].

BPHA is oxidised by potassium permanganate and potassium dichromate in acid medium, but it is quite stable towards hydrogen peroxide[9]. The process of oxidation is very complicated, the reaction is not stoichiometric, and it cannot be employed for quantitative purposes[12].

BPHA is an extremely weak acid, and does not form an ammonium salt when gaseous ammonia is passed through it in ethereal solution[5]. Tsê Yün-hsiang[12] found, by the isosbestic point method and the partition method, that the pK_a for the acid dissociation of BPHA is 7.97 ± 0.11 (at an ionic strength of 1.0); by a two-phase titration method Dyrssen[8] obtained a value of 8.15 ± 0.01 (at an ionic strength of 0.1). The corresponding constant for cupferron is 4.08 ± 0.02 [12] or 4.163 ± 0.007.[8]

The absorption spectrum of BPHA in water has a maximum at 253 mμ with a molar extinction coefficient of 7650.[8] At the isosbestic points (240 and 280 mμ) (Fig. 1) aqueous solutions of BPHA, like those of cupferron (at 235 and 266 mμ), obey the laws of light absorption[12]. According to Dyrssen[8] the partition coefficient of BPHA between chloroform and water is $10^{2.33\pm0.01}$. The value obtained by Tsê Yün-hsiang[12] (216.6 ± 5.0) is 4.5 times his value for the benzene–water system (45.54 ± 0.23). At pH 6 the extractibility of BPHA by chloroform is diminished, owing to dissociation of the BPHA [12] (cupferron starts to dissociate at pH > 3, which also results in a diminution in its extractibility by chloroform); the extractibility of BPHA decreases also in strongly acid medium (>4 *N* with respect to hydrochloric acid)[12].

BPHA reacts with many metal ions to form water-insoluble inner complexes; complex formation takes place by replacement of the hydroxylamino hydrogen by the metal ion with coordination of the carbonyl oxygen

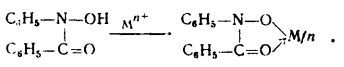


TABLE 3. Qualitative reactions of BPHA with metal ions[12].

Element	Degree of oxidation	Acidity of soln. for pptn.	Colour of ppt.	Colour of chloroform extract
Aluminium	3	pH ~ 3	white	colourless
Antimony	3	pH ~ 1	white	colourless
Antimony	5	~ 3*N*	white	colourless
Beryllium	2	pH ~ 5	white	colourless (floats)
Bismuth	3	pH ~ 3	white	colourless
Cadmium	2	pH ~ 4	white	colourless (floats)
Cerium	3	~ 6	white	colourless
Cerium	4	pH ~ 3*N*	orange	orange
Chromium	3	pH ~ 4	dirty yellow	yellow
Cobalt	2	pH ~ 5	pink	pink
Copper	2	pH ~ 3	yellow – green	yellow – green
Gallium	3	pH ~ 3	white	colourless
Germanium	4	pH ~ 3	white	colourless
Hafnium	4	pH ~ 3*N*	white	colourless
Indium	3	pH ~ 3.5	white	colourless
Iron	2	pH ~ 5	red	red
Iron	3	pH ~ 3	violet	violet
Lanthanum	3	pH ~ 6	white	colourless
Lead	2	pH ~ 4	white	colourless
Manganese	2	pH ~ 6	yellowish	yellowish (floats)
Mercury	1	~ 4	yellow	yellow – green (floats)
Mercury	2	~ 2	yellow	yellow – green (floats)
Molybdenum	6	~ 3	yellowish	yellowish
Neodymium	3	pH > 6	white	colourless
Nickel	2	pH ~ 5	greenish	greenish
Niobium	5	pH ~ 3*N*	white	colourless
Palladium	2	pH ~ 3	orange	pink
Praseodymium	3	pH ~ 6	white	colourless
Samarium	3	pH ~ 7	white	colourless
Scandium	3	pH ~ 3	white	colourless
Tantalum	5	pH ~ 3*N*	white	colourless
Thallium	3	~ 4	white	colourless
Thorium	4	pH ~ 3	white	colourless
Tin	2	~ 3*N*	white	colourless
Tin	4	~ 3*N*	white	colourless
Titanium	4	pH ~ 3*N*	yellow	yellow
Tungsten	6	pH ~ 3	yellowish	yellowish
Uranium	4	pH > 5	orange	yellow
Uranium	6	pH ~ 5	greenish yellow	yellow
Vanadium	5	pH ~ 3*N*	violet – red	violet
Yttrium	3	~ 6	white	colourless
Zinc	2	pH ~ 4	white	colourless (floats)
Zirconium	4	~ 3*N*	white	colourless

Complex formation is greatly dependent on the acidity of the medium. In strongly acid medium (~3 *N* with respect to hydrochloric acid) BPHA precipitates titanium, zirconium, hafnium, vanadium, niobium, tantalum, tin, and antimony; in weakly acid medium (pH 3–6) thorium, scandium, iron, zinc, chromium, aluminium, mercury, rare-earth metals, uranium, cadmium, nickel, copper, gallium, indium, thallium, etc. are precipitated[12].

Benzoylphenylhydroxylamine derivatives of all the elements mentioned, other than antimony, mercury, zinc, and cadmium, are readily extracted by organic solvents (chloroform, isopentyl alcohol). Several elements, for example titanium, vanadium, niobium, quadrivalent cerium, uranium, molybdenum, cobalt, nickel, iron, and copper, form coloured precipitates with BPHA, which dissolve to give correspondingly coloured solutions in organic solvents. Table 3 gives the qualitative reactions of BPHA with various metal ions [12].

The interaction of BPHA with metal ions becomes more selective in the presence of Complexone III†. In its presence at pH 5–6, for example, BPHA precipitates only titanium, vanadium, niobium, molybdenum, tin, uranium, beryllium, aluminium, and iron, other elements remaining in solution [12].

III. USE OF *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE FOR THE QUANTITATIVE DETERMINATION OF ELEMENTS

BPHA is used to determine several elements: aluminium [5], beryllium [13], vanadium [12,14-18], iron [5,12,19], cobalt [20], copper [5], molybdenum [21,22], nickel [20], niobium [23-26], tin [7,10,27], scandium [12,28], tantalum [23,24,26,29], titanium [5,12,26], thorium [30,31], cerium [30], and zirconium [12,32,33]. The methods for determining these elements with BPHA can be divided into three groups — gravimetric, absorptiometric, and titrimetric — among which gravimetric methods are at present outstanding in number and importance.

1. Gravimetric Methods

Aluminium, iron, and copper [5]. Addition of a slight excess of an ethanol solution of BPHA to hot solutions of salts of aluminium, iron, and copper, precipitates these elements as white, red, and yellow-green compounds respectively. The optimum pH ranges for the precipitation of aluminium, iron, and copper are 3.6–6.4, 3.0–5.5, and 3.6–6.0 respectively: at lower pH precipitation is incomplete, while at higher pH somewhat low results are obtained. The resulting precipitates are washed well with hot water, are dried briefly at 110°, and are then suitable for weighing in the gravimetric determination of the three metals. The analyses of the precipitates correspond to the formulae $Al(C_{13}H_{10}O_2N)_3$, $Fe(C_{13}H_{10}O_2N)_3$, and $Cu(C_{13}H_{10}O_2N)_2$. These benzoylphenylhydroxylamine derivatives melt at 238°–239°, 187°–188°, and 198°–199° respectively, are decomposed by mineral acids of moderate concentration, and are readily soluble in organic solvents. In the precipitation of aluminium the concentration of ethanol in the final solution should not exceed 5%, since the aluminium complex, in contrast to the iron and copper derivatives, is quite soluble in aqueous ethanol. Cobalt, cadmium, lead, mercury, manganese, nickel, uranium, zinc, and tartrate, do not interfere with the determination of aluminium, iron, and copper under the above pH conditions; tin, titanium, zirconium, vanadate, molybdate, and tungstate do interfere. The determination of aluminium and iron is impossible also in the presence of phosphate.

† Disodium ethylenediaminetetraacetate dihydrate (Ed. of Translation).

Beryllium [13]. With BPHA beryllium forms a coarse-grained white precipitate having the composition $Be(C_{13}H_{10}O_2N)_2$, which is insoluble in water (up to 70°), relatively insoluble in carbon tetrachloride, acetone, and 50% ethanol, but readily soluble in chloroform. This beryllium complex is decomposed by mineral acids, and melts with decomposition at 220°. Beryllium is quantitatively precipitated by BPHA from hot solutions (50°–60°) at pH 5.0–8.0 and a BPHA concentration of 0.1% (at pH 6.0). The beryllium can be determined either by direct weighing of the precipitate after it has been washed with warm water and dried at 110°, or by weighing beryllium oxide after ignition of the precipitated complex.

Vanadium. With BPHA in strongly acid medium vanadium forms a dark violet compound which is insoluble in water, but which is unsuitable for the gravimetric determination of the metal, since the precipitate is colloidal in character and readily passes through the filter [14]. However, this violet compound can be utilised for the absorptiometric determination of vanadium (see below).

Cobalt and nickel [20]. At pH 5.5–6.5 (in the presence of sodium acetate) BPHA precipitates these metals in the form of a pink and a yellow-green compound respectively. At pH values below the limit mentioned precipitation is incomplete, while lumpy precipitates are obtained at higher pH. The cobalt and nickel complexes can be weighed after being dried at 110°. In the precipitation of cobalt, hydroxylammonium chloride is first added to the solution to be analysed in order to avoid the formation of the tervalent cobalt complex. BPHA is inferior to dimethylglyoxime as a precipitant for nickel, but with cobalt it has the advantage over 1-nitroso-2-naphthol that the benzoylphenylhydroxylamine complex has a perfectly definite composition, and does not require to be subsequently ignited to the oxide or converted into cobalt sulphate.

Molybdenum [21,22]. In the sexivalent state, molybdenum forms with BPHA a yellowish white precipitate of $MoO_2(C_{13}H_{10}O_2N)_2$, which is slightly soluble in hot water (above 80°), in concentrated acids (at lower temperatures), and also in alcohol; the molybdenyl complex decomposes at 165°–166°. Molybdenum is precipitated quantitatively by BPHA from hot solutions (~70°) of acidity 0.01–2.5 *N* (with respect to hydrochloric acid) with a BPHA concentration of 0.03% (below 70°). Molybdenum can be determined either by direct weighing of the precipitate after being dried at 110°–115°, or by weighing molybdenum trioxide after igniting the precipitated complex at 500°–525°. In the presence of cobalt, nickel, or copper the precipitated molybdenyl complex is first washed with 0.2 *N* HCl (as also in the absence of these elements), and then with a 0.02 *N* solution of this acid (instead of water, which is used in the absence of interfering elements); iron(III) and vanadium(V) are masked with Complexone III. BPHA is oxidised by chromium(VI), which therefore interferes with the determination of molybdenum by the first method; tungsten(VI) in acid medium forms a precipitate with BPHA, and strongly interferes with the determination of molybdenum.

Niobium and tantalum. In acid medium BPHA precipitates these metals as white compounds: niobium comes down quantitatively from tartrate solutions starting from an acidity of 2 *N* (with respect to hydrochloric acid) up to pH 6.5; tantalum is completely precipitated only up to pH 1.5. [23,24] Niobium is quantitatively separated from

tantalum at pH 3.5–6.5; while in the presence of Complexone III and tartaric acid, niobium can be determined in the presence of iron, uranium, beryllium, thorium, chromium, aluminium, cerium, copper, cadmium, bismuth, lead, mercury, arsenic, antimony, tin, zinc, manganese, nickel, cobalt, calcium, strontium, barium, magnesium, rare-earth metals, phosphate, chromate, and tungstate; only titanium, zirconium, vanadium, and molybdate interfere. In the gravimetric determination of niobium, the complex is usually ignited to niobium pentoxide [23,24], but it can also be weighed directly (after being dried at 110°) [25], since it has a definite composition $NbO(C_{13}H_{10}O_2N)_3$ and is stable up to 229°. The tantalum precipitate is of indefinite composition, losing weight with rise in temperature, and is unsuitable for direct weighing. Tantalum can be determined in the presence of niobium, titanium, and zirconium by precipitation with BPHA from fluoride-containing solutions acidified with sulphuric acid to pH 1.0 ± 0.1; [29] the optimum temperature for the quantitative precipitation of tantalum lies within the range 5°–27° (it is advisable to keep the solution with the precipitate in cold water for $2\frac{1}{2}$ h before filtering). Good results have been obtained using BPHA for the gravimetric determination of niobium and tantalum in minerals containing titanium, uranium, thorium, and rare-earth metals [26].

Tin. BPHA precipitates tin quantitatively from solutions containing 1–8% conc. HCl. [7] The precipitates isolated from solutions of stannous and stannic salts are white in colour and have the same composition with a melting point of 171°. [7,10] The mechanism of formation and the structure of the tin derivative of BPHA are not known precisely. The compound is stable and is suitable for weighing after being dried at 110°. By means of BPHA tin can be determined gravimetrically in bronzes: copper, lead, and zinc do not interfere [7]. In acid medium (>1% HCl) only tin, vanadium, zirconium, and titanium are precipitated, and therefore BPHA is a selective and the best reagent for tin [10]. It has been recommended as a sensitive reagent for the detection of tin in qualitative semimicro-analysis [27]: in a solution of optimum acidity (0.6 *N* with respect to hydrochloric acid) 0.03 mg tin is easily detected in 1 ml of the final solution by the formation of a readily visible white precipitate.

Scandium [28]. With BPHA, scandium gives a white compound $Sc(C_{13}H_{10}O_2N)_3$, insoluble in water, which separates quantitatively at pH > 5.2 in the presence of a slight excess of the reagent. Thermogravimetric analysis of the scandium precipitate (Fig. 2) showed it to be stable up to 220°; in order to obtain a form of scandium oxide suitable for weighing it is sufficient to heat the precipitate to 600°.

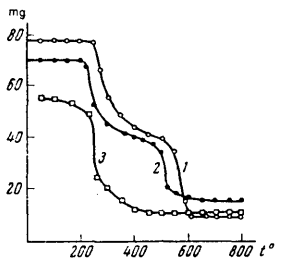


Fig. 2. Thermal decomposition curves for the benzoylphenylhydroxylamine complexes of: 1) scandium; 2) thorium; 3) zirconium.

Titanium. BPHA precipitates titanium as a yellow compound from solutions containing 0.1–0.4 *N* HCl (low results are obtained at higher acidities); it is advisable to carry out precipitation below 25°, since a sticky precipitate is formed at higher temperatures [5]. Langmyhr and Hongslo [26] suggest precipitating titanium from 5% sulphuric acid at 90°, and then cooling the solution and precipitate to 5° in order to precipitate the titanium completely. These workers obtained satisfactory results in the determination of titanium in minerals containing niobium, tantalum, uranium, thorium, and rare-earth metals. The use of BPHA yields good results also in the determination of titanium in ferrotitanium [12] (precipitation being carried out in 1 *N* HCl in the presence of ascorbic acid). The determination is complete by weighing as titanium dioxide, since the precipitate is of indefinite composition.

Thorium. At pH 4.5–5.5 thorium is quantitatively precipitated by BPHA as a white compound, which can be ignited to thorium dioxide [30]. According to Alimarin and Tsê Yün-hsiang [31], the quantitative precipitation of thorium has already begun at pH > 2; the flocculent white precipitate formed initially becomes crystalline after being heated on a water-bath for 5–10 min. The composition of the precipitate deposited from weakly acid solution and dried at 105°–120° is represented by the formula $Th(C_{13}H_{10}O_2N)_4$. Thermogravimetric analysis of the thorium complex (Fig. 2) indicates that it is stable up to 220°; in order to obtain a form of thorium dioxide suitable for weighing, it is sufficient to ignite the precipitate at 650°.

Cerium [30]. Cerium(III) is precipitated quantitatively by BPHA at pH 6.5–7.5 as a white compound; at pH > 7.5 the reagent solution gradually turns red, while at pH < 6.5 the precipitation of cerium is incomplete. Cerium(IV) is precipitated by BPHA at pH 5.0, but the resulting precipitate is gelatinous and is difficult to filter. Cerium(IV) must therefore first be reduced to the cerium(III) with hydroxylammonium chloride. The estimation of cerium is completed by weighing as cerium dioxide after igniting the cerium(III) complex.

Zirconium. According to Alimarin and Tsê Yün-hsiang [32], zirconium is precipitated from hot sulphate or chloride solutions at acidities up to ~3 *N* in the presence of a slight excess of the reagent, as a white compound of composition $Zr(C_{13}H_{10}O_2N)_4$, which is suitable for weighing. Thermogravimetric examination of the precipitate formed under these conditions (Fig. 2) indicates that it is stable up to 240°; in order to obtain a form of zirconium dioxide suitable for weighing, it is sufficient to ignite the precipitate at 500°. According to Ryan [33] the precipitate obtained from chloride solutions, although stable, is not constant in composition (probably owing to the simultaneous precipitation of variable amounts of basic salts, which is prevented in the case of sulphate solutions by the formation of sulphate complexes of zirconium in solution); in this case the precipitate should, in Ryan's opinion, be ignited to zirconium dioxide. The zirconium complex is precipitated quantitatively from sulphate solutions, according to Ryan, only at acidities below 0.5 *N*. The precipitate formed under these conditions has the constant composition $Zr(C_{13}H_{10}O_2N)_4$, is

stable on being heated at 130° for several hours, and is suitable for weighing. The following metals are not precipitated under the conditions of the estimation of zirconium with BPHA: iron, copper, aluminium, bismuth, cadmium, chromium, lead, magnesium, manganese, nickel, zinc, uranium, thorium, yttrium, and rare-earth metals [33]; interference by titanium, cerium(IV), niobium, tantalum, and vanadium [32] is eliminated by masking them with hydrogen peroxide.

2. Absorptiometric Methods

Vanadium. Practically the only element for which a photometric method of estimation using BPHA has been worked out is vanadium. Shome [14] found that, in aqueous ethanol medium at pH 1.9–2.8, BPHA gives with vanadium(V) an orange–red coloration which is suitable for photometric measurement (maximum absorption at 480 mμ). The colour is most stable at pH 2.6, and remains unchanged for 5 h. The sensitivity of the colour reaction is 0.33 mg of vanadium per litre. Many elements (iron, aluminium, titanium, manganese, tungsten, chromium) interfere with the determination of vanadium. Zharovskii and Pilipenko [15] showed that interference by iron and titanium can be avoided by estimating the complex after extracting it with chloroform at pH 5.1–6.0 in the presence of sodium fluoride and phosphoric acid. The chloroform solution of the vanadium complex $V_2O_3(C_{13}H_{10}O_2N)_4$ shows maximum light absorption at 445 mμ (Fig. 3), the molar extinction coefficient being 3600. Satisfactory results in the determination of 0.01–0.3% of vanadium in titanium tetrachloride were obtained, the determination taking 10–15 min. Tsê Yün-hsiang [12] determined vanadium after extracting its complex with a mixture of equal volumes of chloroform and isopentyl alcohol from 0.1–1.5 *N* HCl solutions, and showed that the light absorption of the extracts remains constant for 10 h (maximum absorption at 445 mμ). Ryan [16] showed that it is possible to extract the vanadium complex from more acid media: extraction from 5–9 *N* HCl solutions of vanadate using a chloroform solution of BPHA yields a purple extract having an absorption maximum at 530 mμ (Fig. 4) and a molar extinction coefficient of 4490. The orange extracts obtained from dilute sulphuric-acid solutions of a vanadate also become purple on further acidification with hydrochloric acid. Extraction from strongly acid medium ensures that the photometric determination of vanadium is highly specific: the elements which normally accompany vanadium do not then interfere. Extremely good results have been obtained in the determination of small amounts of vanadium in steels and in chromium ores. Priyadarshini and Tandon [17,18] concluded, from a detailed study of complex formation between vanadium(V) and BPHA, that two complexes are formed in acid medium: a violet complex in strongly acid solutions (>2 M), and an orange–red complex in weakly acid solutions (<0.1 M); the amethyst colour observed at an acidity of 0.1–2.0 M (with respect to hydrochloric acid) results, in their opinion, from the mixing of the colours of the above two complexes (Fig. 5). The violet vanadium complex is readily extracted by chloroform, carbon tetrachloride, ethyl acetate, diethyl ether, benzene, and other organic solvents; all the extracts have an absorption maximum at ~510 mμ. The most suitable extractant is chloroform. At an acidity of 2–10 M (with respect to hydrochloric acid) the position of maximum absorption by the chloroform solution of the complex remains unchanged, but the intensity of absorption remains constant only at 2.8–4.3 M. Beer's law is obeyed (at 510 mμ) at vanadium concentrations of 0.7–12 p.p.m. Even large quantities of aluminium, cobalt, chromium, copper, iron, manganese, nickel, thorium, uranium, zinc, nitrate, and sulphate do not interfere with the determination of vanadium. In the opinion of the above authors, the method is extremely valuable for the direct determination of small quantities of vanadium in ores, alloys, petroleum products, and biological materials.

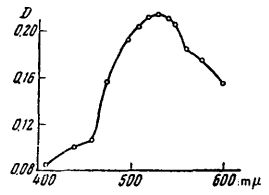


Fig. 4. Absorption spectrum of a chloroform solution of the benzoylphenylhydroxylamine complex of vanadium.

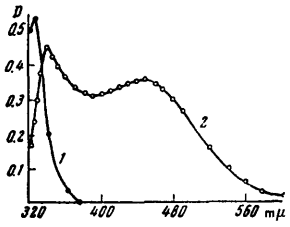


Fig. 3. Absorption spectra of chloroform solutions of: 1) BPHA; 2) BPHA complex of vanadium.

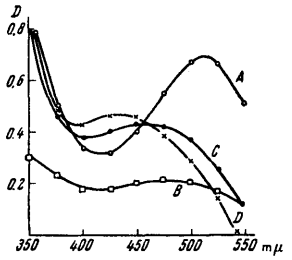


Fig. 5. Absorption spectrum of BPHA–vanadium system in chloroform with various molar concentrations of hydrochloric acid in aqueous phase: *A*) 3.6; *B*) 1.8; *C*) 1.0; *D*) 0.01.

Iron [12]. In aqueous acetone medium (50% acetone) at pH 4–7, iron forms with BPHA a soluble complex which remains stable for a long time and is suitable for the photometric determination of the metal. Beer's law is obeyed for iron concentrations of 0.5–10 μg ml^{-1}; the sensitivity of the reaction is close to that for the sulphosalicylate complex of iron.

3. Titrimetric Methods

This group comprises a small number of methods for determining elements based on the use of BPHA as a complexometric indicator.

Iron. Tervalent iron reacts stoichiometrically with Complexone III at pH 1.0–1.5 and 50°–60°, and can be readily titrated complexometrically at 50° in the presence of 1 ml of a 0.5% acetone solution of BPHA (change in colour from red-violet to lemon yellow or colourless) [19]. The end-point of the titration can be determined either visually or spectrophotometrically (at 500 mμ). Small amounts of cobalt, nickel, copper, aluminium, uranium, and rare-earth metals do not interfere with the titration of iron; but titanium, zirconium, and thorium do interfere. Good results have been obtained in the complexometric determination of iron in iron ores and in magnesite bricks.

Scandium and zirconium. These elements are determined by back-titration of the excess of Complexone III with a ferric solution using BPHA as indicator under the above conditions [12]. The presence of aluminium, beryllium, uranium, and rare-earth metals does not interfere.

IV. USE OF *N*-BENZOYL-*N*-PHENYLHYDROXYLAMINE FOR THE ANALYTICAL SEPARATION OF ELEMENTS

The benzoylphenylhydroxylamine complexes of different elements are quantitatively precipitated from solutions of different acidities, and this makes it possible to use BPHA to separate several elements by precipitation. The selective extraction of the complexes by organic solvents is also used for the separation of elements. In both cases the selectivity of the separation is considerably increased by the presence of masking agents.

1. Separation of Elements by Precipitation

Sinha and Shome [30] found that thorium and cerium(III) are quantitatively precipitated by BPHA at pH 4.5–5.5 and 6.5–7.5 respectively. On this basis they worked out a method for separating thorium and cerium: from a solution containing thorium and cerium(IV), the thorium is first precipitated at pH ~5 by means of BPHA in the presence of hydroxylammonium chloride (to keep the cerium in the tervalent condition); the pH of the solution is then raised with ammonia to ~7, and the cerium is precipitated with the same reagent. Determination of the separated metals is completed gravimetrically by igniting the resulting precipitates to the oxides.

The same workers [20] demonstrated the possibility of separating cobalt or nickel from copper: from a solution containing copper and cobalt, or copper and nickel, the copper is first precipitated with BPHA at pH ~4 (sulphuric acid + sodium acetate), and the the cobalt or nickel at pH 5.5–6.5 (sodium acetate); in the precipitation of cobalt, formation of the cobalt(III) complex is avoided by first adding hydroxylammonium chloride. Determination of the separated metals is effected gravimetrically by the direct weighing of the precipitates.

Majumdar and Mukherjee [23,24] used BPHA in the separation of niobium and tantalum. Their method is based on the precipitation of niobium with BPHA in tartrate medium at pH 3.5–6.5 (ammonium acetate), subsequent lowering of the solution pH to ~1 with sulphuric acid, and precipitation of tantalum at this pH with the same reagent; the separated metals are weighed as their oxides. In the opinion of these workers, a single precipitation is sufficient to separate by this method niobium and tantalum when they are present in proportions varying from 1 : 16 to 100 : 1; when their ratio is 1 : 100, a double precipitation is required. The time necessary for the analysis is considerably less than with other methods.

A slightly modified form of this method [24] was used by Langmyhr and Hongslo [26] in the analysis of mixtures of titanium, niobium, and tantalum. Niobium and tantalum are precipitated together from the test solution by means of BPHA in 1 *N* sulphuric acid, the titanium being kept in solution with Complexone III and hydrogen peroxide. The precipitate is ignited to the oxides and fused with potassium pyrosulphate, for the separation of niobium and tantalum with BPHA; the filtrate is evaporated to decompose the organic compound, and then titanium is precipitated in 5% sulphuric acid medium by means of the same reagent. These workers obtained satisfactory results in the analysis of two complicated minerals, blomstrandine and euxenite, using hydrofluoric acid to decompose the specimens; a single precipitation of titanium, niobium, and tantalum with BPHA in the presence of Complexone III and tartaric acid is sufficient for a preliminary overall separation of these metals from other components of the minerals.

Alimarin and Tsê Yün-hsiang examined the use of BPHA to separate a series of rare elements, and obtained satisfactory results for the separation of scandium from the rare-earth metals and zirconium [28]; thorium from rare-earth metals and uranium(VI); [30] and zirconium from iron, titanium, niobium, and tantalum [32]. In the separation of scandium from rare-earth metals (in proportions from 1 : 5 to 1 : 40) the scandium is first precipitated with BPHA in an acetate buffer at pH 5.2–5.4, and then ammonia is added to the filtrate to precipitate the rare-earth metals as their hydroxides. The separation of scandium from zirconium (in proportions of 1 : 20) is based on the ability of the latter to be precipitated by BPHA in strongly acid medium (2–3 *N* with respect to hydrochloric acid); under these conditions scandium is not precipitated. Thorium is separated from rare-earth metals (in proportions varying from 1 : 10 to 1 : 100) by precipitating it with BPHA in an acetate buffer at pH ~4.5, and from uranium (in proportions between 1 : 4 and 1 : 2000) by precipitation in ammonium carbonate medium at pH 7.0–8.5. Zirconium can be separated from titanium, niobium, and tantalum by precipitating it with BPHA in ~2.5 *N* HCl medium in the presence of hydrogen peroxide, and from iron by precipitation in the presence of ascorbic acid.

BPHA can also be used to separate beryllium from iron, aluminium, and titanium [13]. In this case iron and alumnium (at pH ~4) or titanium (at pH ~1) are first precipitated with BPHA, and then beryllium is brought down from the filtrate (at pH 5.5–6.5) with the same reagent; the precipitate of the beryllium complex is weighed directly after being dried at 110°.

The precipitation of molybdenum(VI) from strongly acid medium (~10 *N* with respect to hydrochloric acid) is used for its separation from cobalt, nickel, and copper, and also from iron(III) and vanadium(V) (in the presence of Complexone III)[22].

2. Separation of Elements by Extraction

The separation of elements by extracting their benzoylphenylhydroxylamine complexes with organic solvents has been little studied. However, preliminary results indicate good prospects for using BPHA as a complexing agent in the extractive separation of elements.

Dyrssen[8] was the first to study the extraction characteristics of BPHA, and he showed that tantalum can be easily separated from uranium and thorium by a single extraction of it, from perchlorate solutions at pH 4.5, with a 0.1 M chloroform solution of BPHA; good separation of uranium and thorium is achieved with a rather greater degree of fractionation. The extraction of lanthanum and uranium is much better with BPHA than with cupferron, which in Dyrssen's opinion is due to the greater stability of the BPHA.

Zharovskii[9] studied the conditions of formation and extraction of the compounds formed by BPHA with cations of Groups III and IV of the analytical tables, and separated several elements (iron, titanium, and vanadium from aluminium; iron from manganese; cadmium from copper; mercury from lead; etc.) by extraction. He worked out a technique for extracting iron and titanium from acid solution (0.5 *N*) with chloroform, and used it to separate these elements from aluminium in the analysis of artificial mixtures and standard specimens of iron ores.

Alimarin and others[12,28,30,34] investigated the effect of the acidity of the solution and the presence of masking agents on the extraction of several metal benzoylphenylhydroxylamine complexes by organic solvents (isopentyl alcohol, chloroform, benzene). The experimental results[12,28] showed that the complexes of titanium, zirconium, hafnium, niobium, and tantalum are extracted in amounts exceeding 90% (single extraction) from a hydrochloric-acid medium (>2 *N*) in the presence of excess of BPHA; the vanadium complex is extracted quantitatively (double extraction) at acidities of 0.1–1.5 *N* (with respect to hydrochloric acid). Other elements, apart from cerium(IV) and tin(II) and (IV), are not extracted in strongly acid media. This makes it possible to separate titanium, zirconium, hafnium, niobium, tantalum, and vanadium from many other elements, for example titanium from iron (in proportions from 1 : 1 to 1 : 3), zirconium from iron (1 : 1 to 1 : 7), zirconium from scandium (200 : 1), vanadium from uranium (1 : 30 to 1 : 20), and niobium from tungsten (1 : 7 to 1 : 70). The ferric, scandium, and thorium complexes are extracted quantitatively by isopentyl alcohol at pH values exceeding 2.5, 4, and 3.5 respectively, whereas the rare-earth metal complexes are not extracted by this solvent at pH 5.8; this forms the basis of extraction techniques for separating scandium and thorium from rare-earth metals (in proportions of 1 : 600 and 1 : 10 respectively)[28,30]. Experiments with radioactive isotopes (niobium-95 and tantalum-182) have shown[34] that, in the presence of tartaric acid at pH 4–6, a single extraction with chloroform removes 98–100% of niobium as its benzoylphenylhydroxylamine complex; tantalum is not extracted at all under these conditions (Fig. 6). Thus rapid separation of niobium and tantalum becomes possible when they are present in proportions ranging from 100 : 1 to 1 : 100. The possibility of separating niobium and tantalum by extraction from fluoride-containing solutions at pH 1 has been mentioned[35].

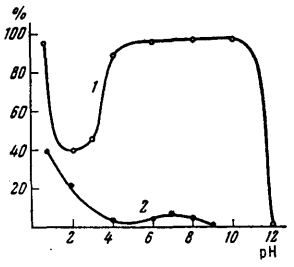


Fig. 6. Effect of pH of aqueous phase on extraction of benzoylphenylhydroxylamine complexes of: 1) niobium; 2) tantalum.

V. DERIVATIVES AND ANALOGUES OF CUPFERRON AS ANALYTICAL REAGENTS

Besides BPHA, several derivatives and analogues of cupferron, all derivatives of hydroxylamine, have been studied for possible analytical applications.

Lutwick and Ryan[10] and also Armour and Ryan[36] prepared and studied a large number of aromatic and acyl derivatives of phenylhydroxylamine and also *N*-benzoyl-*N*-naphthylhydroxylamine and *N*-acetylhydroxylamine. Table 4 gives some physical properties of the compounds investigated. All these compounds are solid crystalline substances which are white in colour — with the exception of *N*-(3,5-dinitrobenzoyl)-*N*-phenylhydroxylamine, which is yellow — and are more or less soluble in water. Many of them melt with decomposition, becoming red or black. Their stability is appreciably greater than that of cupferron: they can be kept for two or more years without appreciable decomposition. All the compounds studied possess in general similar chemical properties, although definite differences exist between them in their ability to react with metal ions in aqueous solutions. In the aromatic phenylhydroxylamines their selectivity towards metal ions increases with increase in acidity of the oxime group of the reagent: in acid solutions (≥1% of acid) only vanadium, tin, titanium, and zirconium are precipitated[10]. With copper as example it has been shown that decrease in the acidity of the reagent is accompanied by an increase in the lower pH limit necessary for complete precipitation of the metal (Table 4). However, a strengthening of the acidic character of the reagent by introducing appropriate substituents results in a decrease in stability of the complexes formed by the reagent. This last statement is true also of acylphenylhydroxylamines[36].

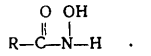
Among the compounds examined only *N*-furoyl-*N*-phenylhydroxylamine, which is able to form an ammonium salt[10], is of some analytical interest. In general, none of the reagents studied possesses any advantages over cupferron or BPHA. The same applies to some other newly investigated reagents: phenylacetylphenylhydroxylamine[37],

TABLE 4. Physical properties of various derivatives of hydroxylamine[10,36].

Substituted hydroxylamine	Colour	M.p., °C	Solubility in water, g per 100 ml	pH of 1% soln. of reagent in ethanol	Lowest pH for complete pptn. of Cu
N-Benzoyl-*N*-phenyl -	white	121	0.040	7.5	3.0
N-*o*-Ethoxybenzoyl-*N*-phenyl-	white	103	0.011	7.3	3.3
N-*o*-Iodobenzoyl-*N*-phenyl-	white	128	0.010	7.3	3.0
N-Naphthoyl-*N*-phenyl-	white	129	0.003	7.2	3.4
N-(3,5-Dinitrobenzoyl)--*N*-phenyl-	yellow	133	0.007	5.8	4.2
N-Furoyl-*N*-phenyl-	white	134	0.013	6.85	3.0
N-(2,4-Dichlorobenzoyl)--*N*-phenyl-	white	137	0.006	6.8	3.7
N-Benzoyl-*N*-naphthyl-	white	164	0.013	4.5	5.5
N-Thenoyl-*N*-phenyl-	white	97		6.85	3.0
N-Nicotinyl-*N*-phenyl-	white	134			
N-Cyclohexanoyl-*N*-phenyl-	white	124		7.25	4.5
N-Hexanoyl-*N*-phenyl-	white	67		7.30	4.5
N-Heptanoyl-*N*-phenyl-	white	60			
N-Acetyl-	white	30			

cinnamoylphenylhydroxylamine[37], phenylazophenylhydroxylamine [3-hydroxy-1,3-diphenyltriazen (Ed. of Translation)][38,39], 2-fluorenylcupferron[40], *p*-phenylcupferron[41-44], and *N*-nitroso-α-naphthylhydroxylamine (neocupferron)[41-44].

More promising compounds from the analytical point of view are the hydroxamic acids



An excellent survey of the literature on the analytical study and application of hydroxamic acids has recently been published by Brandt[45]. A brief survey of various derivatives and analogues of cupferron which are of analytical importance has been given by Macdonald[46,47].

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BPHA, while possessing favourable analytical properties, is stable and will certainly be used in analytical chemistry. The analytical techniques based on its use are simple in execution and effective in results. The possibilities of BPHA as an analytical reagent are far from being exhausted; many types of use are only beginning to be developed, and some of its analytical possibilities have not been studied at all. The analytical study of BPHA is being very vigorously pursued by many investigators.

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RECENT ADVANCES IN THE CHEMISTRY OF THE SESQUITERPENES

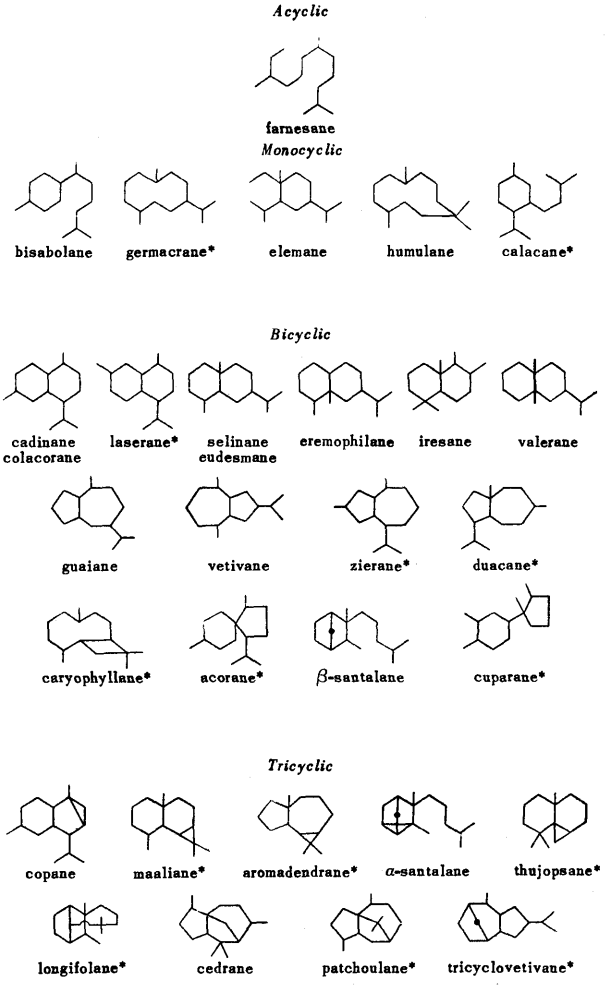
M. Suchý, V. Herout, and F. Šorm

The general study of living matter provides a constant source of information and is of great theoretical and practical value. The very origin of organic chemistry lay in the urge to investigate products of the metabolism of living organisms. Since that time the study of natural products has always formed an important part of organic chemistry. The study of substances contained in plants, which represent the major part (more than 99.9%) of living matter on the earth, has been of especial value in the development of our science. All the types of compound which make up the world of living organisms are produced in plant metabolism; this process is the source of characteristic groups of organic compounds, including especially terpenes, alkaloids, and glycosides. The thorough study of the chemical structure of numerous, genetically interrelated compounds of these groups was stimulated by their biological activity, and sometimes also by their practical importance. Their systematic study contributed to the creation of the best traditions in organic chemistry and to its present diversity.

The study of terpenes and steroids was undoubtedly of great value in the development of organic chemistry. Both groups are restricted by their simple composition, limited by containing only three principal elements, and by the individual structural regularities in each group. However, their great structural diversity and wide distribution was led to the study of terpenes and steroids becoming a subject of deep interest to many laboratories in the world. The principal methods for determining the structure of organic compounds, especially degradation, were discovered and tested in the investigation of compounds of both groups; this simultaneously stimulated the development of synthetic methods. The study of terpenes and steroids laid the foundations of stereochemistry, and constituted the starting points for modern concepts of the spatial structure of organic compounds. Chemistry was simultaneously enriched with very valuable methods for isolating pure organic substances from complex mixtures, and for their determination and identification by means of physical constants or the relations between chemical structure and physical, especially spectroscopic properties, without which modern organic chemistry cannot be imagined.

In our first review paper, published in this journal in 1953,[1] we surveyed the work carried out up to 1952 in the Institute of Organic Chemistry of the Czechoslovak Academy of Sciences. The present paper reviews some later results obtained in the Institute of Organic Chemistry and Biochemistry of the Czechoslovak Academy of Sciences in Prague, especially on terpenoid compounds of the sesquiterpene group which had been little studied previously.

Scheme 1
Survey of types of sesquiterpene hydrocarbons



These compounds, in the study of which great interest has been shown, are very varied. This can be seen from Scheme 1, on which are represented all the hydrocarbon skeletons which have now been established in this group. The asterisks indicate formulae corresponding to structures which have been discovered and proved beyond doubt during the past fifteen years; the remaining structures were investigated earlier. The names of the structural types derive from those of some important sesquiterpenoid hydrocarbons containing the given hydrocarbon skeleton.

The infra-red spectra of the sesquiterpenes and the spectra of their derivatives have been collected in a new volume, which has recently been published by the German Academy of Sciences in Berlin[2].

Those natural products which are sesquiterpene derivatives having a bicyclic five- or seven-membered carbon skeleton and containing a γ-lactone group are worthy of