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PYRAZOLONE DERIVATIVES AS ANALYTICAL REAGENTS

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I. GENERAL REMARKS

Among the organic compounds which form cations and are used in analytical chemistry, the many derivatives of pyrazolone have recently found extensive application – antipyrine, pyramidone, and compounds obtained by condensing antipyrine with various aldehydes and ketones (we shall subsequently refer to these compounds, including pyramidone, as antipyrine derivatives)†. Of the latter, the following are used for the determination of many elements: diantipyrinylmethane, diantipyrinylmethylmethane, diantipyrinylpropylmethane, diantipyrinylphenylmethane, diantipyrinyl-*o*-hydroxyphenylmethane, diantipyrinyl-*p*-hydroxyphenylmethane, diantipyrinyl-*o*-nitrophenylmethane, diantipyrinyl-*p*-dimethylaminophenylmethane, diantipyrinyl-*p*-tolylmethane, diantipyrinylfurylmethane, diantipyrinyl-*p*-hydroxy-*m*-methoxyphenylmethane, antipyrinylbis-(*p*-methylaminophenyl)methane, and antipyrinylbis-(*p*-dimethylaminophenyl)methane. All these compounds in acid solutions are able to form complex organic cations

$$R + H^+ \rightleftarrows RH^+.$$

In the form of these cations they give compounds with many anions, particularly complex ions containing a metal

$$[M^{m+}X_n]^{(m-n)-} + (m-n)\,RH^+ \rightleftarrows (RH^+)_{(m-n)}\,[M^{m+}X_n]^{(m-n)-},$$

where M is a metal, X an electronegative ligand, and R the organic cation.

In neutral or almost neutral media, in which the equilibrium $R + H^+ \rightleftharpoons RH^+$ is displaced to the left, however, antipyrine and its derivatives are able to form compounds of the ammine type:

$$[M^{m+}X_n]^{(m-n)-} + pR \rightleftarrows [M^{m+}R_p]\,X_m + X^-_{(n-m)}.$$

Compounds of this type have been prepared for many metals with antipyrine, pyramidone, and diantipyrinylmethane[1-21]. In the case of the other antipyrine derivatives, the formation of such compounds is evidently hindered by the large size of the amine molecule; this is observed even for the case of complex formation with diantipyrinylmethane[19].

The formation of the various compounds in an R–M–X system depends on the acidity of the medium, the strength of the M–X, M–R, and R–H bonds, and the geometric dimensions of the molecule of the organic cation.

The resulting complexes of both types in a number of cases exhibit valuable properties – low solubility (which ensures a high sensitivity for the reaction), characteristic colour, extractability by organic solvents immiscible with water, etc. This has made it possible to develop gravimetric, titrimetric, photometric, and other methods of determination, and also methods for the separation of many elements.

† We shall not deal with picrolonic acid, 3-methyl-1-phenylpyrazol-5-one, etc., which are not strictly speaking antipyrine derivatives, nor with isopropylantipyrine, antipyrinylmethylenes, etc., which have not yet found extensive applications in analytical chemistry.

Several dyes with antipyrine nuclei have been proposed as analytical reagents: antipyrinylbis-(*p*-methylaminophenyl)methanol, antipyrinylbis-(*p*-dimethylaminophenyl)methanol, and antipyrinylbis-(*p*-benzylmethylaminophenyl)methanol.

In acid solutions they give large organic cations with an intense red colour. Many complex anions containing a metal react with them to form sparingly soluble precipitates. A characteristic feature of these reactions is the change in the colour of the solution during complex formation: the red characteristic of the reagent changes to bright blue, followed by the separation of a blue-violet precipitate and decolorisation of the solution. This colour effect has been used to develop titrimetric methods for the determination of elements forming sparingly soluble compounds with the dyes.

In a number of cases the compounds formed are readily extracted by benzene, ether, and toluene. The colour of the extracts is suitable for spectrophotometric determination. The method has a high sensitivity and in some cases a high selectivity.

Antipyrine and its derivatives listed above (including the dyes with antipyrine nuclei) have been used for the determination or separation of K, Cu, Ag, Au, Ca, Zn, Cd, Hg, Sn, Pb, Ga, In, Tl, the lanthanides, Si, Ti, P, V, As, Sb, Te, Bi, W, U, Re, F, Cl, Br, I, Fe, Co, Ni, Pd, Os, Ir, and Pt. In most cases the methods of determination and separation are based on the formation of onium compounds.

The essential features and possible applications of the proposed methods are examined briefly below.

II. ELEMENTS OF GROUP I OF THE PERIODIC SYSTEM (K, Cu, Ag, Au)

Potassium

Only an indirect method has been described for the determination of K using antipyrine, based on the formation of the green nitrosoantipyrine[22]. Potassium is first separated as $NaK_2[Co(NO_2)_6]$, the precipitate is dissolved, and antipyrine is added to the solution. The potassium content is found from the intensity of the resulting colour. The formation of nitrosoantipyrine is used for the determination of antipyrine and nitrites[23-34].

Copper

In acid solutions in the presence of Cl^-, Br^-, I^-, SCN^-, and CN^- ions, copper reacts with antipyrine and its derivatives to give compounds of the ammonium salt type, of which the compounds with antipyrine and pyramidone have been isolated and analysed[35]. A method has been proposed for the detection of Cu from the formation of the sparingly soluble yellow precipitate with antipyrine or pyramidone in the presence of KI.[36,37]

In acid medium, Cu reacts with antipyrine in the presence of SCN^- ions to form a compound which can be extracted with chloroform to give a violet to brownish violet extract. The reaction is highly sensitive and selective and has been recommended for the detection of Cu.[38]

An analogous reaction is given by pyramidone[38]. Kolthoff and Hamer[39] found that pyramidone reacts with Cu salts in the presence of SCN^- ions to give a grey-blue to violet precipitate. The detectable minimum corresponds to 1 $\mu g\ ml^{-1}\ Cu^{2+}$. At low Cu concentrations the solution is violet[40-43] (oxidation of pyramidone takes place).

It is possible to determine Cu by precipitation and weighing as $(C_{13}H_{17}ON_3.H)[Cu(SCN)_2]$.[35] Compounds of Cu with antipyrine and pyramidone, of the ammine type, have also been prepared[3,4,6,7,9,44], but they have not found analytical application.

Silver

$AgNO_3$ oxidises pyramidone with the formation of the violet colour characteristic of the product of the oxidation of pyramidone and the separation of a grey-black precipitate of metallic silver[30-33]. The reaction can be used for the detection of Ag or pyramidone.

Gold

A method has been described for the detection of small quantities (0.01 mg) of Au in the form of the sparingly soluble chloroaurate of antipyrine[45]. The chloroaurate of diantipyrinylmethane has been isolated from acid solutions in the form of red-brown crystals[46].

III. ELEMENTS OF GROUP II OF THE PERIODIC SYSTEM (Ca, Zn, Cd, Hg)

Antipyrine and its derivatives have not been used for the determination of Mg, Sr, and Ba, although compounds of the ammine type formed by these elements with antipyrine and pyramidone are known[4,6-8].

Calcium

An indirect method for the determination of calcium using antipyrine, based on the formation of nitrosoantipyrine, has been described[47]. Ca is first separated as $K_2CaNi(NO_2)_6$. The nitrite in the resulting precipitate is determined photometrically with antipyrine.

Zinc

In acid solutions in the presence of SCN^- ions, zinc reacts with antipyrine and its derivatives to form sparingly soluble compounds of the type $(RH)_2[Zn(SCN)_4]$. The compound with antipyrine has been proposed for the qualitative detection of Zn.[39,48,49] The precipitate can be detected at a concentration of 100 $\mu g\ ml^{-1}$ Zn. Precipitation with pyramidone makes it possible to detect 6–7 $\mu g\ ml^{-1}$ Zn in the presence of Ba, Ca, Mg, Sr, Al, Mn, As, and Cd, if the reaction is carried out in acetic acid[50-52].

Zhivopistsev[53] established that the compound of Zn^{II} with pyramidone, $(C_{13}H_{17}ON_3.H)_2[Zn(SCN)_4]$, is isomorphous with the analogous cobalt compound $(C_{13}H_{17}ON_3.H)_2.[Co(SCN)_4]$. In the presence of Co, the Zn precipitate is coloured blue by the Co, which undergoes isomorphous coprecipitation. In this case it is possible to detect 0.2 μg Zn.

The compound of Zn with pyramidone is readily obtained in the pure form, has a constant composition, and had been used to standardise solutions of Complexone III‡.[54]

The precipitation of Zn with pyramidone has also been used for the micro-crystalloscopic detection of pyramidone[55]. Diantipyrinylmethane has been used to purify Ni, Mn, Al, and Cr salts from Zn.[56]

The compound formed by Zn with diantipyrinylmethane is readily soluble in chloroform. This feature has been used for the determination of Zn in highly pure nickel, after preliminary extraction with chloroform (Ni remains in the aqueous phase)[57].

Gusev and Bitovt[58-61] found that the compound of Zn with diantipyrinylmethylmethane at pH 2–2.5 forms a stable white turbidity which makes possible the nephelometric determination of 0.12–2 μg of Zn in the presence of the cations of analytical groups I and II, and also Al, Mn, Fe^{III}, Cu, Ni, and Co respectively. The method has been used to determine Zn in industrial atmospheres, alloys, foodstuffs, blood, and other materials.

Zhivopistsev[62] proposed that the precipitation of $Zn(SCN)_4^{2-}$ ions with antipyrinylbis-(*p*-dimethylaminophenyl)methane be used for the detection of small quantities (0.1–0.28 $\mu g \times \times ml^{-1}$) of Zn.

Sparingly soluble bright blue precipitates $(RH)_2[Zn(SCN)_4]$ are formed by Zn in acid solutions with antipyrinylbis-(*p*-methylaminophenyl)methanol and antipyrinylbis-(*p*-dimethylaminophenyl)methanol (the detectable minimum corresponds to 0.2–0.3 μg and 2–3 μg of Zn respectively)[63,64]. It has been shown possible to determine Zn gravimetrically as $(C_{29}H_{32}O_2N_4)_2[Zn(SCN)_4]$. The error in the determination of 5–20 mg of Zn does not exceed 3–4%.[65] The determination of Zn can be completed photometrically after dissolving the precipitate in 1 *N* HCl. The error in the determination is 2–4%.[66] A titrimetric method has been developed for the determination of Zn using antipyrinylbis-(*p*-dimethylaminophenyl)methanol[67]. The error in the determination of 0.001–0.03 g of Zn amounts to 2–3%. In neutral or almost neutral solutions Zn forms a compound of the ammine type, $Zn(R)_2(SCN)_2$.

Zhivopistsev[68] has developed a titrimetric method for the determination of Zn using pyramidone. The method has been used to determine Zn in alloys of the "Elektron" type [Mg-base alloys (Ed. of Translation)].

Cadmium

In acid solutions, cadmium gives sparingly soluble compounds $(RH)_2[CdX_4]$ with antipyrine§ and its derivatives, not only in the presence of SCN^- ions as in the case of Zn, but also in the presence of Br^- and I^- ions.

Precipitation by antipyrine in the presence of Br^- and I^- ions has been proposed for the detection of Cd and antipyrine[36,37,69,70]. When the reaction is carried out in the presence of bromides, it is possible to detect 50 $\mu g\ ml^{-1}$ Cd. Gusev[70] developed a gravimetric method for the determination of Cd as $(C_{11}H_{12}ON_2.H)_2[CdBr_4].2C_{11}H_{12}ON_2$. Korenman and coworkers[71,72] studied the completeness of

‡ Sodium salt of EDTA (Ed. of Translation).

§ In the case of antipyrine, the compound $(C_{11}H_{12}ON_2H)_2.[CdBr_4].2C_{11}H_{12}ON_2$ is formed.

precipitation of Cd as antipyrine tetrabromocadmate¶ and the possible coprecipitation of Fe^{3+}, Zn^{2+}, and Hg^{2+} ions with the Cd precipitate, and established that the precipitation of Cd is not quantitative and that Fe^{3+}, Zn^{2+}, and Hg^{2+} are coprecipitated.

The determination of Cd can be completed not only by weighing the precipitate but also iodometrically or by titration with alkali and Methyl Orange after dissolving the antipyrine tetrabromocadmate precipitate[73]. The iodometric method is based on the formation of iodopyrine. The excess of iodine is titrated with thiosulphate.

The compound of Cd with pyramidone $(C_{13}H_{17}ON_3 \cdot H)_2 \cdot [CdI_4]$ has been recommended for the detection of Cd (> 3.64 μg ml^{-1}) and pyramidone (the detectable minimum corresponds to 5 μg of pyramidone in one drop of solution)[51,55]. The precipitate is also suitable for the gravimetric determination of Cd in the presence of small quantities of Zn.[35] Diantipyrinylmethane precipitates Cd quantitatively from 0.5–2.0 N H_2SO_4 solutions as $(C_{23}H_{24}O_2N_4 \cdot H)_2 \cdot [CdBr_4]$. The formation of diantipyrinylmethane tetrabromocadmate has been made the basis of gravimetric[74-77], potentiometric[78], and amperometric[79] methods for the determination of Cd.

In the presence of iodides, an even less soluble compound of Cd with diantipyrinylmethane is formed; this has been used for the determination of small quantities (0.002–0.0001%) of Cd in highly pure nickel[80].

Diantipyrinyl-*o*-hydroxyphenylmethane also precipitates Cd quantitatively as $(C_{29}H_{26}O_3N_4 \cdot H)_2[CdBr_4]$. The precipitate has a definite composition and is suitable for the gravimetric determination of Cd[81].

The dyestuffs antipyrinylbis-(*p*-methylaminophenyl)-methanol and antipyrinylbis-(*p*-dimethylaminophenyl)-methanol react with Cd in acid medium in the presence of SCN^- or I^- ions to form sparingly soluble compounds which, as in the case of Zn, are suitable for the qualitative and quantitative determination of Cd.[64,67].

A method has been developed for the detection of Cd in the presence of Cu and also Al, Mn, Cr, Ni, Co, Fe, As, and the alkali and alkaline earth metals, using antipyrinylbis-(*p*-benzylmethylaminophenyl)methanol, which reacts with Cd in acid medium to give a precipitate of $(C_{40}H_{39}ON_4)_2 \cdot [CdBr_4]$.[82] The drop method makes it possible to detect 0.01 μg of Cd.

Compounds of the ammine type have also been used for the determination of Cd. A method has been developed for the gravimetric determination of Cd by precipitation and weighing as $[Cd(C_{13}H_{17}ON_3)_2](SCN)_2$.[83]

Popel'[79] obtained good results in the amperometric titration of Cd with $(NH_4)_2[Hg(SCN)_4]$ solution in the presence of antipyrine or pyramidone.

A method has been proposed for the amperometric determination of Cd, based on the formation of a sparingly soluble precipitate of $(C_{13}H_{17}ON_3)_2[CdI_2]$† at pH 2–5 in the presence of an excess of pyramidone. The titration is carried out with KI solution from the cathodic Cd current.

The successive determination of Bi (titration in 4.5–6 N H_2SO_4) and Cd (titration at pH 2–5) has been shown to be possible. The method was tested on alloys containing Cd and Bi, together with Zn, Al, and Mn.[84]

Mercury

Antipyrine, pyramidone, antipyrinylbis-(*p*-methylaminophenyl)methanol, antipyrinylbis-(*p*-dimethylaminophenyl)methanol have been used for the qualitative and quantitative determination of Hg.

Antipyrine and pyramidone form compounds with Hg^I and Hg^{II} in the presence of Cl^-, Br^-, I^-, CN^-, NO_3^-, and SCN^- ions[85-92]. Mercury is precipitated by antipyrine from acidic solutions in the presence of KI as $(C_{11}H_{12}ON_2 \cdot H)_2[HgI_4]$ (sensitivity 4 μg ml^{-1} Hg,[93] limiting dilution 1 : 200 000 [36,37]).

In dilute solutions, a stable turbidity suitable for the nephelometric determination of Hg is formed[93].

Antipyrine tetraiodomercurate is readily extracted by chloroform from 0.3–1.3 N H_2SO_4, HCl, or HNO_3 solutions. The colour of the extracts can be used for the spectrophotometric determination of 1–80 μg of Hg in 5 ml of solution at $\lambda = 330$ mμm.[94]

In the presence of bromides, the compound $(C_{11}H_{12}ON_2 \cdot H)_2[HgBr_4] \cdot 2C_{11}H_{12}ON_2$ is formed. Cd, Zn, and Fe^{III} are coprecipitated, but in a number of cases the coprecipitation is slight and cannot influence the accuracy of the gravimetric determination of Hg as antipyrine tetrabromomercurate[72,95].

The coprecipitation of Cd with the Hg precipitate can be used for the separation of small quantities (20–70 μg) of Cd from solutions of Zn and Cu salts[96].

Sudo[97] showed that the antipyrine–thiocyanato-complex of Hg is extracted quantitatively from weakly acidic (pH 1.8–2.3) solutions by a 3 : 1 mixture of pentanol and ethyl acetate. The optical density of the extracts ($\lambda = 325$ mμm) is proportional to the Hg concentration in the range 5–40 μg ml^{-1}.

Zhivopistsev[98] developed a titrimetric method for the determination of Hg using antipyrinylbis-(*p*-dimethylaminodiphenyl)methanol, based on the precipitation of $[HgI_4]^{2-}$ by the dyestuff from 0.7–1.5 N HCl solutions. The method can be used to determine 0.0003–0.06 g of Hg with an error of 3–4%.

Hg can also be determined with antipyrinylbis-(*p*-methylaminophenyl)methanol, which forms an even less soluble compound with $[HgI_4]^{2-}$ (the detectable minimum corresponds to 0.6 μg Hg).[64]

A method for the detection of Hg using pyramidone is based on the oxidation of pyramidone by mercury(II) (the blue-violet product of the oxidation of pyramidone is formed). The detectable minimum corresponds to 20 μg Hg.[99] The reaction can be used to distinguish the Hg_2^{2+} cation from the Hg^{2+} cation.

IV. ELEMENTS OF GROUP III OF THE PERIODIC SYSTEM (Ga, In, Tl, lanthanides)

Gallium

Gallium is precipitated from acidic solutions in the presence of Cl^-, Br^-, and I^- ions by diantipyrinylmethane,

¶ We shall use this terminology, since it is widespread in the literature, although it would be more correct to refer to these as "antipyrinium" salts.

† This is presumably a compound of the ammine type (Ed. of Translation).

diantipyrinylpropylmethane, and diantipyrinylphenylmethane. A gravimetric method has been developed for the determination of Ga as $(C_{26}H_{30}O_2N_4.H)[GaCl_4]$.[100]

The compound of Ga with diantipyrinylphenylmethane is extracted quantitatively by chloroform and this has been used for the separation of Ga from Al, Zn, Cd, Pb, Bi, As, Fe, Cu, In, and Ge by extraction[101].

Ga reacts with the dyestuffs to form the compounds $RHGaCl_4$, which are readily extracted by toluene and chloroform[102]. The use of antipyrinylbis-(*p*-benzylmethylaminophenyl)methanol has been proposed for the spectrophotometric determination of Ga. Ga is extracted from 6 *N* HCl to the extent of 90%. The sensitivity corresponds to 0.2 $\mu g\ ml^{-1}$ Ga. The method is applicable to the determination of Ga in bauxites, alumina, and copper–zinc ores.

Indium

In sulphuric acid solutions (~0.5 *N*) in the presence of SCN^- ions, indium reacts with antipyrine, pyramidone, and diantipyrinylmethane to form sparingly soluble compounds $[In_2(R)_3](SCN)_6$.[103] The compound with antipyrine has the composition $[In(C_{11}H_{12}ON_2)_3](SCN)_3$. The least soluble compound is that formed with diantipyrinylmethane. It has been shown possible to determine In gravimetrically as $[In_2(C_{23}H_{24}O_2N_4)_3](SCN)_6$.

A nephelometric method has been developed for the determination of microgramme quantities (0.5–1.0 $\mu g\ ml^{-1}$) of In.

Thallium

Tervalent thallium in acid medium in the presence of Cl^-, Br^-, and I^- ions reacts with antipyrine and its derivatives to form sparingly soluble compounds $(RH)[TlX_4]$. The compound of $TlBr_4^-$ with antipyrine has the composition $(C_{11}H_{12}ON_2.H)[TlBr_4].C_{11}H_{12}ON_2$.

The compound with antipyrinylmethane $(C_{23}H_{24}O_2N_4.H).[TlBr_4]$ has been used for the gravimetric determination of Tl^{III} in the presence of Cu, Zn, PO_4^{3-}, AsO_4^{3-}, and also Fe, Bi (after their conversion into the complexonates) and Sb (converted beforehand into the tartrato-complex)[104]. The method has been used to determine Tl^{III} in its alloys with Sb, As, or P.[105]

The determination of Tl^{III} as $(C_{23}H_{24}O_2N_4.H)[TlBr_4]$ can be finished titrimetrically[105]. Diantipyrinylpropylmethane has been recommended for the precipitation of Tl^{III} from hydrochloric acid (1–6 *N*) solutions[106]. The precipitate has a definite composition corresponding to the formula $(C_{26}H_{30}O_2N_4.H)[TlCl_4]$, is sparingly soluble ($5.6 \times 10^{-5}$ M), and is suitable for the gravimetric determination of Tl^{III}. The method has been used to determine Tl^{III} in cadmium.

Diantipyrinyl- and diantipyrinylpropyl-methane tetraiodothallates are readily extracted by benzene with the formation of yellow extracts (λ = 400–405 mμm, ϵ = 12 000)[107]. The extraction-photometric determination of Tl^{III} is possible in the presence of Fe, Bi, Cu, Zn, Cd, Pb, Ga, and In. The minimum detectable quantity corresponds to 0.3 $\mu g \times \times ml^{-1}$ Tl.

An extraction-photometric method for the determination of Tl^{III} using antipyrinylbis-(*p*-dimethylaminophenyl)methanol has also been proposed[108]. The method is based on the formation of a compound by $TlCl_4^-$ and the dyestuff, readily extracted by a 2 : 3 mixture of benzene and CCl_4.

In weakly acidic solutions Tl^{III} oxidises pyramidone with the formation of a blue-violet compound. After 30 min the solution (pH 3.5–4.5) becomes red (λ = 510 mμm) and this colour is preserved for 50–100 min. Kamemoto[109] has used this for the colorimetric determination of Tl^{III}. The method makes it possible to determine 0.5–4.5 mg Tl in 50 ml solution.

The Lanthanides

These react with antipyrine and pyramidone to form compounds of the ammine type[5,10,11]. The solubilities and rates of formation of the compounds differ. Marsh[110,111] has used this feature to separate the lanthanides by fractional crystallisation; he showed that in the form of the compounds $[M(C_{11}H_{12}ON_2)_6]I_3$, Lu and Tu, Lu and Er, Lu and Yb, and Y and Ho are readily separated; Ho, Dy, and Tb are less readily separated; and Pr and Nd are not separated.

V. ELEMENTS OF GROUP IV OF THE PERIODIC SYSTEM (Ti, Si, Ge, Sn, Pb)

Titanium

In hydrochloric acid (0.5–6 *N*) or sulphuric acid solutions, titanium reacts with diantipyrinylmethane to form a yellow compound (λ = 385 mμm, ϵ = 15 000). The molar ratio of Ti to diantipyrinylmethane in the complex is 1 : 3.[112] The compound is an ammine‡. Thus in 0.01–2 *N* HCl solutions the complex $[Ti(C_{23}H_{24}O_2N_4)_3]^{4+}$ exists[114].

The solutions obey Beer's law in the range 1–3 $\mu g\ ml^{-1}$ Ti. Ti can be determined spectrophotometrically in the presence of Fe^{II}, Al, Cd, Hg, Zn, and the alkali and alkaline earth metals; fluorides and phosphates do not interfere[115]. The method is 20 times more sensitive than the peroxide method and has the advantage over the chromotropic acid method that it does not require strict observation of the reaction conditions (pH, etc.). The method has been used to determine small quantities of Ti (0.0001–0.00005%) in aluminium and magnesium[116], and also to determine Ti in the presence of V in heat-resistant nickel- and iron-base alloys[117].

In the presence of thiocyanates, Ti reacts with diantipyrinylmethane to give a complex which is readily extracted from hydrochloric acid solutions by chloroform. On this basis a method has been developed for separating Ti from Al and Fe with subsequent determination as TiO_2.[118]

The composition of the complex formed in an excess of SCN^- ions corresponds to the formula $[Ti(C_{23}H_{24}O_2N_4).(SCN)_4]$.[114,119] The chloroform extracts (λ = 420 mμm, ϵ = 60 000) are suitable for the spectrophotometric determination of 2–20 μg Ti in 25 ml extract[120].

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‡ Compounds of the ammonium salt type have been isolated from chloroform solutions and analysed: $(C_{23}H_{24}O_2N_4.H)_2[TiCl_6]$ and $(RH)_2[Ti(SCN)_6]$. The compounds $(RH)[TiO(SCN)_3]$, where R = diantipyrinylpropyl-, diantipyrinylisobutyl-, and diantipyrinylphenyl-methane[113], have been isolated from aqueous alcohol solutions.

In hydrochloric acid or sulphuric acid solutions, Ti^{III} and Ti^{IV} react with diantipyrinyl-*o*-hydroxyphenylmethane to give readily soluble inner-complex compounds. The Ti^{III} compound has an intense yellow colour. The solutions are suitable for the qualitative and quantitative determination of Ti.[121] The minimum detectable quantity corresponds to 0.35 $\mu g\ ml^{-1}$ Ti. The spectrophotometric method can be used to determine 2–30 $\mu g\ ml^{-1}$ Ti.

The salts of the diantipyrinyl-*o*-hydroxyphenylmethane complex of Ti^{IV} with NO_3^-, ClO_3^-, SCN^-, and ClO_4^- ions are sparingly soluble and separate as characteristic crystalline precipitates suitable for the qualitative detection of Ti.[122-124]

Antipyrine has also been used to precipitate the tannin complex of Ti. The antipyrine-tannin method has been used to determine small quantities (0.1–0.01 g) of Ti in the presence of Fe, Al, and Cr.[125] The reaction has been proposed for the detection of Ti by the spot method[126].

Silicon

Silicon in the form of molybdosilicic and tungstosilicic acids is precipitated from acid solutions by antipyrine and pyramidone in the form of the sparingly soluble compounds $(C_{13}H_{17}ON_3)_3H_8Si(Mo_2O_7)_6.6H_2O$,[127,128] $4C_{11}H_{12}ON.SiO_2.12WO_3$, and $3C_{13}H_{17}ON_3.SiO_2.12WO_3$.[129] A method has been developed for the gravimetric determination of Si as pyramidone molybdosilicate[128]. The other compounds have been used for the amperometric[129-132] and titrimetric[133] determination of antipyrine and pyramidone. The methods developed can probably be used no less successfully for the determination of Si or W.

Germanium

Germanium is precipitated from acid solutions as the sparingly soluble antipyrine or pyramidone molybdogermanates[134]. It has been shown possible to determine Ge gravimetrically as the antipyrine compound. Pyramidone molybdogermanate can be used to develop a vanadometric method for the determination of Ge by titration of the excess of pyramidone after separation of the precipitate. The vanadometric method for the determination of pyramidone makes it possible to determine 0.004–0.02 g of pyramidone with an error of ±3%.[135]

Tin and Lead

Tin and lead react with antipyrine and its derivatives to give sparingly soluble compounds[36,37,52,56,57,62,136-140]. The compound formed by Sn with antipyrine in the presence of KI has been used to detect Sn after separation from interfering elements as the sulphide[141].

VI. ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM (P, V, As, Sb, Bi)

Phosphorus

Molybdophosphoric or tungstophosphoric acids are precipitated by antipyrine and pyramidone from acid solutions. The compounds have been used for the spectrophotometric[142-144] and amperometric[130,131] determination of antipyrine and pyramidone and also for the detection of phosphoric acid[145].

Gusev[146] proposed a nephelometric method for the determination of phosphates, based on the formation of a stable turbidity when ammonium molybdate and antipyrine are added to a nitric acid (~ 2 *N*) solution of the phosphates. The method can be used to determine 0.05 $\mu g\ ml^{-1}$ P with an error of ±10%.

Vanadium

Vanadium has been determined using diantipyrinylphenylmethane by precipitation and weighing as $(C_{29}H_{28}O_2N_4)_2H_4V_6O_{17}$ (or as V_2O_5 after ignition of the precipitate)[147].

Sokolova[148] has proposed a spectrophotometric method for the determination of V using pyramidone. The method is based on the formation of a blue solution by the reaction of pyramidone with V and tungstophosphoric acid in Na_2CO_3 solution. The detectable minimum corresponds to 0.3 $\mu g\ ml^{-1}$ V. Beer's law is observed in the range 0.6–30 $\mu g\ ml^{-1}$.

Arsenic

Arsenic(V) in nitric acid solutions in the presence of ammonium molybdate reacts with antipyrine to form a stable turbidity, which is suitable for the nephelometric determination of As.[149] The method makes it possible to determine 0.1–2 $\mu g\ ml^{-1}$ As with an error of ±10%.

Antimony

Antimony(III) reacts with antipyrine in acid solution in the presence of KI to give a yellow precipitate[141,150-153]. The sensitivity corresponds to 25 $\mu g\ ml^{-1}$ Sb and the limiting dilution is 1 : 20 000 (according to Korenman 1 : 40 000[36,37]). In dilute solutions (0.2 *N* with respect to HCl) a stable turbidity is formed, shown by Gusev[154] to be suitable for the nephelometric determination of 2.5 $\mu g\ ml^{-1}$ Sb in the presence of 75 $\mu g\ ml^{-1}$ Sn^{2+}. The error in the determination does not exceed ±5–6%.

The complex of Sb with antipyrine is readily extracted by chloroform. The coloured extracts (λ = 345 mμm) can be used for the spectrophotometric determination of 1–100 μg Sb.[155]

Diantipyrinylmethane precipitates Sb quantitatively even at low concentrations of KI in the solution (0.1 M); from very dilute solutions antimony is coprecipitated quantitatively with the sparingly soluble diantipyrinylmethane iodide. This has been used for the separation and subsequent polarographic determination of microgramme quantities (5×10^{-9} g litre^{-1}) of Sb.[156]

Bismuth

In acid solutions in the presence of Cl^-, Br^-, I^-, and SCN^- ions, bismuth(III) reacts with antipyrine and its derivatives to form the compounds $(RH)[BiX_4]$, sparingly soluble in water. The reaction is highly sensitive. Thus precipitation of BiI_4^- makes it possible to detect Bi at a dilution of 1 : 2 000 000 using antipyrine, or 1 : 48 000 using pyramidone[36,37,157,158].

The formation of pyramidone tetraiodobismuthate has been made the basis of nephelometric [159], amperometric [160], and heterometric (by Bobtelsky and Cohen) [161,162] methods for the determination of Bi and also for the titrimetric determination of pyramidone [163].

The nephelometric method based on the formation of a stable turbidity in dilute nitric acid solutions makes it possible to determine 0.5 μg ml^{-1} Bi in the presence of 0.1 mg ml^{-1} Sb, 0.015 mg ml^{-1} Pb, and 10 mg ml^{-1} Sn with an error of ±3–7%.

The amperometric determination is carried out by titrating sulphuric acid (2.5 M H_2SO_4) solutions of the Bi salt with potassium iodide in the presence of pyramidone, from the cathodic Bi current at a dropping mercury electrode.

The heterometric titration of nitric acid (~ 0.5 N) solutions of $Bi(NO_3)_3$ with pyramidone solution (in the presence of KI) or with KI solution (in the presence of pyramidone) can be used to determine ~ 1 mg Bi.

The titrimetric determination of pyramidone using potassium iodobismuthate involves the precipitation of pyramidone with standard $KBiI_4$ solution with subsequent titration of the excess of Bi with Complexone III until the disappearance of the yellow of the potassium iodobismuthate solution. The formation of the sparingly soluble compound with diantipyrinylmethane $(C_{23}H_{24}O_2N_4.H)[BiI_4]$ was used by Zhivopistsev and Parkacheva [164] to develop a titrimetric method for the determination of Bi. The method can be used to determine 80–50 mg Bi with an error of 2–3%.

A gravimetric method for the determination of Bi using diantipyrinylmethane by precipitation and weighing as $(C_{23}H_{24}O_2N_4.H)[BiCl_4]$ has been proposed [165]. The precipitation is carried out from hydrochloric acid (0.5–2.0 N) solutions; the error in the determination is 2–3%.

The compounds of Bi with antipyrine and diantipyrinylmethane are readily extracted by various organic solvents with the formation of coloured extracts suitable for the spectrophotometric determination of Bi.

Sudo [94,155] developed an extraction-photometric method for the determination of Bi using antipyrine in the presence of SCN^- or I^- ions. In the first case, Bi is extracted from weakly acidic solution (pH 1.8–2.3) by a 1 : 4 mixture of pentanol and ethyl acetate. The optical density of the extracts is measured at 325 mμm. The method makes it possible to determine 1–100 μg Bi in 5 ml solution.

In the second case (in the presence of KI) the extraction is carried out with chloroform. Measurement of the optical density of the extracts at 500 mμm makes it possible to determine 1–50 μg Bi in 5 ml solution.

In the presence of diantipyrinylmethane, BiI_4^- ions are readily extracted by chloroform over a wide range of acidity (up to 3 N with respect to HCl or H_2SO_4) of the original solution [166]. The colour of the extracts can be used for the photometric determination of 20–30 μg Bi in 25 ml.

VII. ELEMENTS OF GROUP VI OF THE PERIODIC SYSTEM (Te, W, U)

Antipyrine and its derivatives have not yet been used for the determination of Cr and Mo. Compounds of Cr^{III} with antipyrine [6,7] and of Cr^{VI} (as $Cr_2O_7^{2-}$) with diantipyrinylphenylmethane [167] have been prepared. The addition of pyramidone solution to potassium dichromate solution produces a dark green which changes to wine red [168,169].

Tellurium

In acid solutions tellurium(IV) reacts with the antipyrine derivatives diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane to give compounds of the type $(RH)_2[TeCl_6]$ and $(RH)_2[TeBr_6]$, which are readily extracted by dichloroethane to give coloured extracts [170]. On this basis, a method has been developed for the extraction-photometric determination of tellurium. The method makes it possible to determine 10–100 μg ml^{-1} Te.

Se^{IV}, unlike Te^{IV}, is not extracted from hydrochloric acid solutions by dichloroethane in the presence of diantipyrinylpropylmethane. This has been used for the separation of Se and Te by extraction. A single extraction gives almost complete separation of 0.05–2 mg of Se and Te. [171]

Tungsten

In acid solutions, tungsten forms sparingly soluble compounds with antipyrine [172–176], pyramidone [177–180], diantipyrinylphenylmethane [181], diantipyrinyl-*o*-hydroxyphenylmethane [182], and various other antipyrine derivatives. These reagents have been used for the gravimetric determination of W. In all cases the determination is finished by igniting the precipitates and weighing the resulting WO_3. The accuracy of the proposed methods is no less than the classical cinchonine method, but is more rapid and uses more readily available reagents.

Uranium

In sulphuric acid solutions in the presence of SCN^- ions, uranium in the form of uranyl nitrate reacts with antipyrine and some of its derivatives to form sparingly soluble compounds with variable composition [183]. At low U concentrations the compound with diantipyrinyl-*p*-dimethylphenylmethane gives a stable turbidity which is suitable for the nephelometric determination of U. The method makes it possible to determine 0.5–5 μg UO_2^{2+} in the presence of 2.5 mg La^{3+}.

In the presence of bromides, uranyl nitrate reacts with diantipyrinyl-*p*-hydroxy-*m*-methoxyphenylmethane with the formation of yellow compound. Maximum development of the colour is observed at pH 2–3. The extraction-photometric method makes it possible to determine 5–60 μg × × ml^{-1} UO_2^{2+} in the presence of appreciable quantities of Th^{4+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, and Cu^{2+}. The error in the determination amounts to ±3.5%. The method is suitable for the determination of uranium in various minerals (samarskite, aeschynite, sooty uranite, etc.).

VIII. ELEMENTS OF GROUP VII OF THE PERIODIC SYSTEM (Mn, Re, F, Cl, Br, I)

Manganese

Compounds of Mn^{II} with antipyrine, of the ammine type, have been prepared [6] but these have not been used for the determination of Mn.

Rhenium

Re in the form of perrhenate and chlororhenate forms sparingly soluble compounds with antipyrine [184].

Fluorine

Čelechovsky and Holer [185] developed a photometric method for the determination of fluorides, based on the decolorisation of the red solution of the Fe^{III}–antipyrine complex in the presence of fluorides. The method makes it possible to determine 35–300 μg F in 25 ml solution. The error in the determination is 3.1–4%.

Chlorine, Bromine, and Iodine

These oxidise pyramidone with the formation of a blue-violet colour [186]. The reaction with I has been recommended for the detection of pyramidone [186].

In the presence of I^- ions and also Br^-, SCN^-, and $S_2O_3^{2-}$ ions, the copper–pyramidone complex is decomposed with the formation of the salt of Cu with the corresponding anion; the solution is coloured violet by the product of the oxidation of pyramidone [43]. The reaction has been recommended for the detection of iodides. The sensitivity corresponds to 3.2 μg ml^{-1} I^- (limiting dilution 1 : 12 500).

Antipyrine has also been used to combine with the iodine liberated in the determination of iodides using iodate [187].

IX. ELEMENTS OF GROUP VIII OF THE PERIODIC SYSTEM (Fe, Co, Ni, Pd, Os, Ir, Pt)

Iron

In hydrochloric acid, sulphuric acid, acetic acid, and neutral solutions, iron(III) reacts with antipyrine to form a red compound readily soluble in water. This was observed at an early date by Knorr [23], who was the first to prepare antipyrine. The reaction is fairly sensitive (according to Knorr the limiting dilution is 1 : 100 000) and suitable for the qualitative and quantitative determination of Fe and antipyrine [24,26,28,30–33,188,189]. The complex formed is of the ammine type. The compound $(C_{11}H_{12}ON_2)_3.FeCl_3$ has been prepared in the crystalline state [190]. The addition of $K_4[Fe(CN)_6]$ solution to a solution containing Fe^{3+} and antipyrine gives an immediate dark red precipitate of $[Fe(C_{11}H_{12}ON_2)_3][Fe(CN)_6].3H_2O$. Analogous compounds have been obtained with other complex anions: $[Fe(CN)_5.(NH_3)]^{2-}$, $[Co(CN)_6]^{3-}$, and $[Fe(CN)_5(NO_2)]^{2-}$ [191,192]. This indicates that in solution Fe^{III} reacts with antipyrine to form the complex cation $[Fe(C_{11}H_{12}ON_2)_3]^{3+}$.

Other authors [189] report the formation of the cation $[Fe_2(C_{11}H_{12}ON_2)_3]^{6+}$. Compounds confirming the possible formation of this cation have been prepared in the crystalline state: $[Fe_2(C_{11}H_{12}ON_2)_3][Fe(CN)_5(NO_2)]_3$ [191] and $(C_{11}H_{12}ON_2)_3.2FeCl_3$. [32,33,193,194]

In the presence of SCN^- ions the red sparingly-soluble compound $[Fe(C_{11}H_{12}ON_2)_3](SCN)_3$ is formed [191,194,195].

Sudo [196] established that the complex of Fe^{III} with antipyrine is readily extracted from weakly acidic solutions (pH 2.5) in the presence of SCN^- ions by certain organic solvents. The best of these is a 4 : 1 mixture of ethyl acetate and isobutanol. The red extracts are suitable for the spectrophotometric determination of Fe. The method has been used to determine small quantities (0.0002%) of Fe in the metals aluminium, magnesium, zinc, and lead. The error in the determination is < 5%. [197]

Dick [198] found that from acetic acid solutions containing an excess of thiocyanate ions, Fe^{III} is precipitated quantitatively as $[Fe(C_{11}H_{12}ON_2)_3](SCN)_3$. The sensitivity of the reaction corresponds to 0.2 μg Fe.

In acid medium, antipyrine forms with $K_4[Fe(CN)_6]$ the sparingly soluble compound $(C_{11}H_{12}ON_2)_2H_4[Fe(CN)_6]$. [190,199,200] Hexacyanoferrate(III) does not form a compound of this type and this has been used to identify $[Fe(CN)_6]^{4-}$ in the presence of $[Fe(CN)_6]^{3-}$. [201]

The reaction of $K_4[Fe(CN)_6]$ with antipyrine was used by Gusev [51] for the titrimetric determination of antipyrine involving titration of the excess of $K_4[Fe(CN)_6]$ with $KMnO_4$ solution after separation of the precipitate.

Diantipyrinylmethane, like antipyrine, reacts with Fe^{III} in hydrochloric acid solutions to form a red complex. The number of diantipyrinylmethane molecules entering the resulting compound depends on the acidity of the medium [202]. Thus at pH 1–2 the complex $Fe(C_{23}H_{24}O_2N_4)_2^{3+}$ is formed. In 1 *N* HCl solutions the cation $Fe(C_{23}H_{24}O_2N_4)^{3+}$ predominates. The solutions of the complex (λ = 440–460 mμm), formed at pH 2.2–2.5, are suitable for the spectrophotometric determination of Fe. [203] The sensitivity of the reaction corresponds to 0.08 μg ml^{-1} Fe.

Zhivopistsev and Chelnokova [204] found that Fe^{III} is extracted quantitatively from strongly acidic (5–7 *N* HCl) solutions by chloroform in the presence of diantipyrinylmethane. In this case a compound of Fe^{III} with diantipyrinylmethane, of the ammonium salt type, is probably formed. A method was developed [204] for the quantitative separation and subsequent determination (from the colour of the extracts in the case of small quantities, or as Fe_2O_3 after re-extraction with water in the case of large quantities) of Fe from Ti, Cr, Ni, Al, Mn, and Mg, using diantipyrinylmethane and chloroform.

In the presence of SCN^- ions, coloured compounds $Fe(C_{23}H_{24}O_2N_4)_3(SCN)_3$ (pH 2, λ = 455 mμm, ε = 10 000) and $(C_{23}H_{24}O_2N_4.H)_3[Fe(SCN)_6]$ (1 *N* HCl, λ = 475 mμm, ε = 35 000), readily extracted by chloroform, are formed [202]. This forms the basis of a method proposed by Zhivopistsev [205] for the extraction-photometric determination of Fe. The detectable minimum corresponds to 0.04–0.05 μg Fe. In the presence of Co the determination of Fe can be finished using *o*-phenanthroline after re-extraction with acetate buffer solution (pH 5.37). [206]

Iron is coprecipitated quantitatively in the form of the diantipyrinylmethane–thiocyanato-complex with diantipyrinylmethane thiocyanate. This has been used to purify Ni, Mn, Al, and Cr salts from Fe. [56] Thus after the precipitation, nickel contains < 0.0002% Fe.

Diantipyrinylphenylmethane, unlike antipyrine, precipitates $[Fe(CN)_6]^{3-}$ ions from sulphuric acid solution and gives no precipitate with $[Fe(CN)_6]^{4-}$. The precipitate has a definite composition corresponding to the formula $(C_{29}H_{28}O_2N_4.H)_3[Fe(CN)_6]$ and is suitable for the gravimetric determination of cyanoferrate(III) in the presence of cyanoferrate(II), and also for the determination of cyanoferrate(II) after oxidation to $[Fe(CN)_6]^{3-}$. [167]

In acid medium in the presence of SCN^- ions, antipyrinylbis-(*p*-dimethylaminodiphenyl)methane reacts with

Fe^{III} to form a sparingly soluble compound[62]. The reaction is extremely sensitive (0.02–0.03 μg ml^{-1} Fe).

Diantipyrinylfurylmethane in acid medium reacts with $Fe(SCN)_3$ to give a red compound which is sparingly soluble in water and readily soluble in acetone. The acetone solutions are suitable for the spectrophotometric determination of 0.3–1 μg ml^{-1} Fe.[207]

It is also possible to determine Fe using pyramidone. The proposed methods are based on the oxidation of pyramidone by Fe^{III} with the formation of an intense blue-violet colour. The detectable minimum corresponds to 0.1 μg ml^{-1} Fe.[188,208] In the acidity range 0.1–0.2 *N* HCl the colour of the solution depends little on the acidity, and the spectrophotometric determination of 0.5–3.0 μg ml^{-1} Fe is possible[209].

The reaction has also been used to identify $[Fe(CN)_6]^{3-}$ in the presence of $[Fe(CN)_6]^{4-}$ [210,211] and for the determination of pyramidone[30-33,47,212].

Cobalt

In acid solutions in the presence of SCN^- ions, cobalt(II) reacts with antipyrine§ and its derivatives to form blue compounds $(RH)_2[Co(SCN)_4]$ which are sparingly soluble in water but readily soluble in certain organic solvents. The compound with antipyrine has the composition $(C_{11}H_{12}ON_2.H)_2[Co(SCN)_4].2C_{11}H_{12}ON_2$.[215]

The formation of antipyrine tetrathiocyanatocobaltate has been recommended as a sensitive and selective reaction for the detection of Co.[38,48,215,216]

Antipyrine tetrathiocyanatocobaltate is readily extracted from weakly acidic solutions (pH 1.8–2.2) by a 5 : 1 mixture of ethyl acetate and benzene[217]. The coloured extracts (λ = 630 mμm, ϵ = 3156) can be used for the spectrophotometric determination of 1–100 μg of Co in 5 ml.

The formation of pyramidone tetrathiocyanatocobaltate is highly sensitive (the detectable minimum corresponds to 1 μg Co) and has been used for the detection of Co in nickel[218,219] and for the identification of pyramidone[55]. Zhivopistsev[220] has suggested that the reaction be carried out in the presence of Zn^{2+} ions, which react with pyramidone to give the compound $(C_{13}H_{17}ON_3.H)_2[Zn(SCN)_4]$, isomorphous with the compound $(C_{13}H_{17}ON_3.H)_2[Co(SCN)_4]$. In this case the Co compound does not form supersaturated solutions (which is the case at low Co^{2+} contents) and the sensitivity of detection increases: the white Zn precipitate is coloured blue in the presence of as little as 0.4 μg Co.[2]

The compound of Co with diantipyrinylmethane $(C_{23}H_{24}O_2N_4.H)_2[Co(SCN)_4]$ has been recommended by Zhivopistsev for the detection[74] and quantitative determination[221] of Co. The spot test method has been used to detect 0.06 μg Co in the presence of Cr, Ni, Fe^{II}, Mn, Al, Zn, and the alkali and alkaline earth metals. The complex is readily extracted by chloroform with the formation of a blue extract. The colour of the extracts can be used for the spectrophotometric determination of Co in the presence of the elements indicated above. The error in the determination is 1 μg at a Co content less than 10 μg ml^{-1}, and 2 μg at a Co content of 10–50 μg ml^{-1}. The method has been used to determine small quantities (0.1–1.25%) of Co in steels containing up to 20% Ni.[222]

In the presence of Fe or Cd, which are also readily extracted in the form of compounds with diantipyrinylmethane, the determination of Co can be finished using nitroso-R-salt after re-extraction with acetate buffer solution. This method has been used to determine 0.0007% Co in pure nickel[206]. Ikramov[223] has made a comparative study of the diantipyrinylmethane and nitroso-R-salt methods for the determination of Co.

Diantipyrinylmethane has also been used for the detection of SCN^- ions (the detectable minimum corresponds to 0.13 mg ml^{-1}).[224]

Equally sensitive reactions with Co in the presence of SCN^- ions are given by diantipyrinylmethylmethane, diantipyrinylpropylmethane, diantipyrinyl-*o*-hydroxyphenylmethane, and diantipyrinyl-*p*-hydroxyphenylmethane (sensitivity 7.5 μg Co in 2 ml); less sensitive reactions are given by diantipyrinyl-*p*-tolylmethane (10 μg Co), diantipyrinyl-*o*-nitrophenylmethane (15.0 μg Co), and diantipyrinyl-*p*-dimethylaminophenylmethane (20.0 μg Co)[225]. All these reagents, like diantipyrinylmethane, are suitable for the photometric determination of cobalt from the blue colour of the benzene extract. The optimum acidity corresponds to 0.02 *N* H_2SO_4. The error in the determination of 0.06–0.1 mg Co in 2–5 ml of extract does not exceed ±10%. The method has been used for the determination of Co in bronze and cast iron.

A titrimetric method has been proposed for the determination of Co using pyramidone, based on the formation, at pH 5–6, of the complex $Co(C_{13}H_{14}ON_3)_2(SCN)_2$, which is sparingly soluble in water[226].

Nickel

From acetic acid solutions in the presence of pyramidone and NH_4SCN, nickel is precipitated as $[Ni(C_{13}H_{17}ON_3)_2].(SCN)_2$. The precipitate is almost insoluble in solution containing an excess[227] of the reagents and is suitable for the gravimetric determination of Ni and pyramidone[228,229]. The sensitivity corresponds to 10 μg ml^{-1} Ni.

Palladium

In acid solutions, palladium(II) reacts with antipyrine and diantipyrinylmethane to form complexes which are readily extracted by chloroform with the formation of coloured extracts. On this basis, Sudo[94] developed a spectrophotometric method for the determination of Pd using antipyrine. The optimum acidity of the solution corresponds to 0.3–1.5 *N* HCl or H_2SO_4, or 0.3–1.0 *N* HNO_3. The method can be used to determine 1–20 μg Pd in 5 ml of extract.

Kreimer and coworkers[230] proposed the use of antipyrinylmethane instead of antipyrine. The optical density of the extracts was measured at 450 mμm. The sensitivity corresponds to 0.43 μg ml^{-1} Pd. The method was used for the determination of 0.01–0.05% Pd in the products of nickel manufacture, containing up to 40% Ni, 20% Cu, and 5% Fe.

§ A spot test for the detection of Co^{2+} using antipyrine has been described, based on the formation of a blue-green or pale green (depending on the Co content) colour, developed by drying a strip of filter paper moistened first with Co^{2+} solution and then with 20–30% antipyrine solution[213,214].

Palladium is readily extracted from hydrochloric acid (0.5–5 *N* HCl) solutions with dichloroethane in the presence of diantipyrinylpropylmethane (with a sixfold excess of the reagent the degree of extraction of Pd is >99%). This has been used to remove traces of Pd from Rh.[231,232]

Compounds of Pd with antipyrine and pyramidone have also been prepared: $(C_{11}H_{12}ON_2.H)_2[Pd(CN)_4]$, $(C_{13}H_{17}ON_3.H_2)_2[Pd(SCN)_4]$, and $(C_{11}H_{12}ON_2.H)_2[PdCl_4].2H_2O$.[233–235] No practical use has been made of these compounds, however,

Osmium

In acid solutions, osmium in the form of $OsCl_6^{2-}$ or $OsBr_6^{2-}$ reacts with antipyrine, diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane to form the compounds $(RH)_2[OsCl_6]$ and $(RH)_2[OsBr_6]$.[236] A method has been proposed for the gravimetric determination of osmium by precipitation and weighing as $(C_{23}H_{24}O_2N_4.H)_2.[OsBr_6]$ and $(C_{26}H_{30}O_2N_4.H)_2[OsCl_6]$.[237] The method can be used to determine 5–13 mg Os with an error of ±3%.

Os^{IV} is readily extracted by dichloroethane, with the formation of coloured extracts, from hydrochloric and hydrobromic acid solutions (0.5–5 *N*) containing diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane. On this basis a method has been developed for the extraction-photometric determination of Os using diantipyrinylpropylmethane[238,239].

Os^{IV} is extracted from hydrochloric acid (0.5–5 *N*) solutions with a 0.1% solution of the reagent in dichloroethane. The optical density of the extracts (λ = 346 mμm, ϵ = 10 500; λ = 378 mμm, ϵ = 8000) is measured relative to a solution of the reagent saturated with 1 *N* HCl. The method can be used to determine 2–20 μg ml^{-1} Os in the presence of 40 mg Ru with an error of ±10%.

Iridium

In acid solutions, iridium in the form of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ reacts with antipyrine, diantipyrinylmethane, diantipyrinylpropylmethane, and diantipyrinylphenylmethane to give the compounds $(RH)_2[IrCl_6]$ and $(RH)_2[IrBr_6]$.[240]

The compound formed by iridium with diantipyrinylpropylmethane is sparingly soluble in water (the solubility in 0.5 *N* HCl amounts to 3.8×10^{-5} M) and has been used for the gravimetric determination of iridium by precipitation and weighing as $(C_{26}H_{30}O_2N_4.H)_2[IrCl_6]$. The error in the determination of 5–13 mg Ir amounts to ±3%.

The complex of Ir^{IV} with diantipyrinylpropylmethane is readily extracted by dichloroethane with the formation of a coloured extract (the degree of extraction for a tenfold excess of the reagent amounts to 98.5%). On this basis a method has been developed for the extraction-photometric determination of 4–40 μg ml^{-1} Ir using diantipyrinylpropylmethane[231,232].

Platinum

Platinum(IV) is readily extracted by dichloroethane from hydrochloric acid (0.5–6 *N*) solutions in the presence of diantipyrinylpropylmethane (the degree of extraction with a sixfold excess of the reagent is greater than 99%).[231,232] This has been used for the separation of traces of Pt from Rh by extraction.

Compounds of Pt with antipyrine, pyramidone, and diantipyrinylmethane have also been prepared: $(C_{11}H_{12}ON_2.H)_2[PtCl_6]$,[199] $(C_{11}H_{12}ON_2.H)_2[PtCl_4]$, $(C_{11}H_{12}ON_2.H)_2[Pt(CN)_4]$,[234,235] $(C_{13}H_{17}ON_3.H)_2[PtCl_6]$,[239] and $(C_{23}H_{24}O_2N_4)H_2[PtCl_6]$.[46] These compounds have not, however, found application in analysis.

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