ANALYTICAL STUDY OF THE BASIC PROPERTIES OF LEAD TETRAACETATE AS OXIDIZING AGENT

J. Zýka

Department of Analytical Chemistry, Charles University,
Prague, Czechoslovakia

INTRODUCTION

Among tetravalent lead compounds having the character of lead(IV) acids, lead tetrahalides of the type PbX_4 (X = halogen), lead(IV) sulphate and lead tetraacetate are currently known. For oxidation purposes particularly in the case of organic compounds, lead tetraacetate has found the widest use; it has replaced oxidations with, for example, lead dioxide not only in preparative reactions but especially in the case of the analytical applications of such processes.

Lead tetraacetate was prepared for the first time more than a hundred years ago by Jaquelain[1], and studied as far as its oxidation effects are concerned, by Dimroth and collaborators[2, 3], who found that lead tetraacetate is a more selective oxidizing agent as compared to the lead dioxide used previously.

Criegee and coworkers[4–10] have reported the characteristic effect of lead tetraacetate on α-glycols and substances of related structure, in which the bond between the carbon atoms is split. Lead tetraacetate oxidizes the same types of compounds as periodic acid and its salts, the products obtained with these two agents being also the same. Oxidations with lead tetraacetate have been dealt with in a review by Fleury and Courtois[11].

Lead tetraacetate and periodic acid react differently with α-monohydroxy acids and some *cis –trans* isomers of α-glycols. Whereas periodic acid oxidizes α-monohydroxy acids at room temperature slowly, their oxidation with lead tetraacetate is generally rapid and quantitative. Periodic acid oxidizes *cis* and *trans* isomers of α-glycols equally rapidly. On the other hand, lead tetraacetate oxidizes the *cis* isomers more rapidly than the *trans* forms, and for this reason it is used frequently to distinguish between the two forms.

Since oxidations with lead tetraacetate proceed very rapidly, they may be used for indirect determinations of α-glycols and of substances of similar character, either the reagent excess or the oxidation products formed being determined, similarly as in oxidations with periodic acid and its salts. Unlike periodic acid and its salts, lead tetraacetate oxidizes, in many cases, even the oxidation products, although at a slow rate. Another fact which must be considered in lead tetraacetate oxidations is the necessity of using an excess of it in a non-aqueous medium (mainly in glacial acetic acid) in order to eliminate hydrolysis of the lead(IV) salt. Acetic acid, liberated during the reduction of the reagent by its oxidative effect according to the equation

$$Pb(CH_3COO)_4 + 2\,H^+ + 2e \rightarrow Pb(CH_3COO)_2 + 2\,CH_3COOH$$

usually makes the determinations based on determining oxidation products of acid character difficult. For a long time it has been recommended that acetic anhydride should be added to lead tetraacetate solutions (prepared by dissolving the pure substance, or by the reaction of red lead (Pb_3O_4) with glacial acetic acid) in order to secure a perfectly anhydrous medium. The anhydride, however, reacts with the reagent (Tomíček and Valcha[12]), reducing the effectiveness of lead tetraacetate solutions. This has led to the erroneous opinion that the reagent itself is of low stability. The authors mentioned have proved that lead tetraacetate solutions in glacial acetic acid in the absence of acetic anhydride are stable, and may well be used for volumetric purposes. In all volumetric determinations with lead tetraacetate solution carried out up to recent times it has been stressed that the medium must be kept strictly anhydrous in order to hinder the possible hydrolysis of lead(IV) salts, although it is known that the presence of water increases the rate of oxidation with lead(IV) salts. Only a few years ago, when we started to study oxidations with lead tetraacetate systematically, did we find that it is possible to titrate with this reagent even in aqueous solutions, possibly in the presence of mineral acids, determining in this manner inorganic as well as organic systems[13–22]. A necessary condition for such titrations, of course, is that the oxidation of these systems must proceed more rapidly than the hydrolysis of lead(IV) salts. We have found recently that numerous substances similar in character to vicinal glycols, or those having a similar structure, may be determined by means of an excess of the reagent even in aqueous solutions of 50 to 80 per cent acetic acid in the presence of alkaline acetate[18–22]. The unreacted amount of lead tetraacetate is titrated potentiometrically with a standard hydroquinone solution. The advantage of this method lies in the fact that the oxidation of substances to be determined proceeds rapidly in comparison with other reagents and quantitatively to carbon dioxide or the respective aldehyde,

Table 1. Values of Pb^{IV}/Pb^{II} formal redox potentials in some mineral acids. (Values given are in mV, compared to a standard hydrogen electrode: values are means of several measurements)

Acid	*Molarity*	*Formal redox potential* (mV)
Hydrochloric acid*	0·03	1390
	1	1290
	2	1270
	4	1210
Perchloric acid†	1	1660
	2·3	1670
	3·4	1660
	5·8	1690
	8·4	1830
	11·0	1910
Phosphoric acid‡	0·7	1550
	1·4	1480
	3·5	1300
	7·0	1220

* In solutions of $<0{\cdot}03$N HCl hydrolysis of lead(IV) salts take place, in 4N HCl solutions oxidation liberates free chlorine.

† In solutions of <1N $HClO_4$ hydrolysis of lead(IV) salts take place.

‡ In solutions of $<0{\cdot}7$ M H_3PO_4 lead(II) phosphate precipitates. At concentrations of >7M H_3PO_4 the potential stabilizes very slowly.

even at room temperature, and the reaction may be used for microanalytical purposes.

OXIDIMETRIC DETERMINATIONS WITH LEAD TETRAACETATE

The present review summarizes results obtained in a study of those properties of reagent mentioned, which may be significant for its further application in analytical chemistry and for the elucidation of the oxidative effect proper of lead(IV) compounds, examples are given of its present application in oxidimetric determinations of inorganic and organic compounds.

As stated in the following paragraphs and in *Table 1*, lead tetraacetate may be classified among the very efficient oxidimetric reagents, being suitable for direct volumetric determinations, mainly with potentiometric indication, as well as for indirect oxidations, utilizing its excess.

Preparation

Lead tetraacetate may be prepared (*i*) by the reaction of red lead (Pb_3O_4) with anhydrous acetic acid—a substantial amount of lead diacetate is also formed—the lead(II) salt may be separated making use of its lower solubility in glacial acetic acid; (*ii*) by oxidation of lead diacetate with gaseous chlorine, again in a medium of glacial acetic acid; the $PbCl_2$ formed is removed by filtration; (*iii*) for volumetric purposes we recommend the reagent to be prepared by dissolving red lead (Pb_3O_4) in glacial acetic acid at elevated temperatures; the lead tetraacetate crystals formed are isolated, recrystallized and the required amount is dissolved in a known volume of glacial acetic acid; solutions thus prepared contain no lead(II) salts[14], and if kept in dark-coloured stock bottles will remain stable for periods of several months. Their stability is decreased substantially by the presence of acetic anhydride or alkaline metal acetates. Due to the great volume changes of glacial acetic acid with temperature variations, conditions used must be such that the temperature does not vary within a range of more than $\pm 1\,^{\circ}C$ during the analysis.

Determination of titre value

With regard to determining the titre value of the volumetric lead tetraacetate solutions, one of the following methods may be followed—potentiometric titration with: (*i*) a hydrazine sulphate standard solution[13]; (*ii*) hydroquinone[12] whose titre is pre-determined by means of dichromate; (*iii*) a standard ferrocyanide solution[34]. We have found titration of a known amount of thallous salt[19] as the best for determining the titre value of dilute lead tetraacetate solutions used in microtitrations (0·01 N and more dilute solutions). Among visual methods we might mention the classical iodometric determination (using an excess of potassium iodide and sodium acetate followed by titration of the iodine liberated with thiosulphate).

An interesting possibility is the use of a standard solution of an arsenous salt for the visual determination of the titre value of lead tetraacetate solutions. When a lead tetraacetate solution is added to a standard arsenic(III) solution in the presence of an excess of potassium iodide and starch solution as indicator, the iodide is first oxidized to iodine, which immediately continues to oxidize the arsenous to the arsenic salt. When all the arsenic has been converted to the pentavalent form, the first excess drop of the reagent marks the end of the titration by the characteristic reaction of the liberated excess iodine with starch. Notwithstanding the relatively low differences of the redox potentials of the systems $2\,I^-/I_2$ (0·622 V) and $AsO_3{}^{3-}/AsO_2{}^-$ (0·56 V) the reaction proceeds rapidly and in a quantiative way. This is due to the fact that the lead(II) salt formed by reduction of lead tetraacetate reacts with the arsenate formed by the oxidation, giving the low-soluble lead(II) arsenate, which favourably influences the reaction equilibria and shifts them in suitable directions. The titration is carried out in the presence of sodium acetate, which forms a buffer solution with the acetic acid added in the reagent solution. Although it is known that sodium bicarbonate is the best medium for the oxidation of arsenic(III) salts with iodine, the reaction proceeded in our case quantitatively even in a weakly acid medium, probably due to the formation of the above-mentioned lead(II) arsenate[23a]. No universally suitable indicator has yet been found for direct titrations with lead(IV) salts, and potentiometric (sometimes amperometric[35]) indication of the point of equivalence is used; quinalizarin[12] has been proposed as indicator for the titration of benzylmercaptan in non-aqueous medium. N,N-bis-4-(4-methoxyphenylamine)phenyl thiourea[12a] has been proposed for the titration of ascorbic acid.

Theoretical considerations of oxidimetric determinations with lead tetraacetate

It has been found that lead tetraacetate is suitable for the oxidimetric determination of a number of inorganic and organic systems as evidenced by numerous communications in the literature. A survey of these determinations is given in *Table 2* and the most important explications in the text, as well as in the reviews[22a, 32, 33] and in the monographs[36–38]. It is significant that varying opinions have been advanced concerning the oxidation mechanism using lead tetraacetate. Nonetheless little attention has been given to the study of this problem, or to the study of the basic properties of lead tetraacetate solutions, which might be important for further development of their use, *e.g.* problems of the formal oxidation–reduction potentials of the system Pb^{IV}/Pb^{II} in various acids, its polarographic behaviour, spectra, etc. We have attempted to contribute to the solution of these problems by some of our investigations. For the normal oxidation–reduction potential of $Pb^{4+} + 2e \rightleftarrows Pb^{2+}$, Latimer[42] states a value of 1·7 V.

Formal reduction potentials

As to the formal redox potentials, Charlot's tables[43] mention a value of 1·8 V for a medium of 1–8 M HNO_3, as the mean value of data by several authors who have measured the potential of a platinum electrode in a mixture of $PbO_2 + Pb^{II}$ in the acid mentioned.

Tomíček and Valcha[12] have studied the formal redox potentials of the system Pb^{IV}/Pb^{II} in the case of lead tetraacetate and diacetate in glacial acetic acid medium. In some cases in the presence of alkaline metal acetates

Table 2. Substances capable of being determined with lead tetraacetate as volumetric reagent

---

As^{3+}
Sb^{3+}
Sn^{2+}
Fe^{2+}
Ti^{3+}
Cr^{2+}
Tl^{+}
Mo^{III}, Mo^{V}
U^{III}, U^{IV}
Ru^{VI}
Eu^{2+}
H_2O_2 + perioxidic substances
I^-, I_2, I^+
Br^-
$[Fe(CN)_6]^{4-}$
NO_2^-
$N_2H_4.H_2SO_4$
$S_2O_3^{2-}$
Phenylhydrazine chloride
p-Nitrophenylhydrazine
Isonicotinic acid hydrazide
Semicarbazide chloride

Ascorbic acid
Hydroquinone
Pyrocatechol
Cysteine
Thiourea
Thiosemicarbazide
n-Butylmercaptan
sec-Butylmercaptan
Benzylmercaptan
Di-*n*-butylsulphide
Di-*sec*-butylsulphide
tert-Butyl-*sec*-butylsulphide
tert-Butyl-*n*-butylsulphide
Di-*tert*-butylsulphide
tert-Butyl-isobutylsulphide
n-Butylphenylsulphide
Diphenylsulphide
Dibenzylsulphide
1,4-Anhydroxythritol
Methyl-Δ-D-mannofuranoside
1,4-Anhydromannitol

Methyl-2,6-anhydro-Δ-D-altro-pyranoside
Formic acid
Tartaric acid
Mandelic acid
Malic acid
Citric acid
Ethylene glycol
Tetrachlorohydroquinone
Diallylbarbituric acid*
Allylisopropylbarbituric acid*
Crotonic acid*
Oleic acid*
Erucic acid*
Salicylic acid*
Glycerol
Mannitol
Calcium gluconate
Ricinic oil (iodine number)*
Rape oil (iodine number)*
Olive oil (iodine number)*

---

* Titrated with bromine, generated by tetraacetate as volumetric agent, from excess bromide.

they found values of not more than 1·32 V; with addition of perchloric acid values of the order of 1·44 V were obtained. In our experiments carried out in aqueous solutions and in media of various mineral acids (values determined either from the course of the potentiometric titration of a suitable system with lead tetraacetate, or by measuring the potential of a platinum electrode in an equimolar mixture of lead tetraacetate–lead diacetate in the respective mineral acid) we found, that in acetic acid medium the redox potential is greatly dependent on the concentration of this acid and on the concentration of the Pb^{IV} and Pb^{II} components present, and that it varies with time, a fact which might be ascribed to the formation of lead tetraacetate complexes with water. In solutions containing less than 30 per cent acetic acid the value of the formal redox potential of the system measured is 1·45 V, in solutions containing 0·4 M sodium acetate, irrespective of the concentration of acetic acid present the redox potential is about 0·1 V lower[23]. As to the formal redox potentials and their values mentioned in the following paragraphs it must be stated that although the measurement has been carried out in the medium of the given mineral acid, a certain amount of acetic acid must be considered in every case, as this is brought into the solution automatically with the lead tetraacetate solution. This amount, however, is practically negligible if we consider it in comparison with the large mineral acid excess forming the main component of the medium. The measurement could not be performed in sulphuric acid medium, in which $PbSO_4$ is precipitated, nor in nitric acid medium, in whose presence Pb^{IV} hydrolysis immediately takes place.

In a medium of hydrochloric acid we have found, that the value of the formal redox potential Pb^{IV}/Pb^{II} is 1·39 V, in 0·03 N HCl, decreasing continuously to a value of 1·21 V in a medium of 4 N HCl (see *Table 1*). In perchloric acid medium in a wide range of concentrations of this acid, no great differences of formal redox potential values are observed in the range of 1 to 6 N $HClO_4$. In general, potentials are high in this medium, rising from about 1·66 V in 1 N $HClO_4$ up to 1·91 V in 11 N $HClO_4$. Measurement of the formal redox potentials in phosphoric acid medium has shown, that in the range of 0·7 to 7 M H_3PO_4 their values decrease from the lowest to the highest acid concentration, from 1·55 V to 1·22 V. Measurements in this acid, however, were rather difficult to perform compared to the preceding acids. From the measurements it follows that lead tetraacetate, considering the values of formal redox potentials, is amongst the most efficient oxidation agents. The highest values of formal redox potentials are achieved in perchloric acid medium. It is interesting to note that in the range of 1 to 3 N $HClO_4$ its value practically does not change. We have compared the experimental values with the theoretical value calculated from the Peters equation, using data given in the literature for E: $Pb^{IV}/Pb^{II} = 1{\cdot}7$ V (with activity coefficient values of 0·95 and 0·85 for a unit ionic strength) assuming that in 1 M $HClO_4$ lead tetraacetate and diacetate are fully dissociated. The value calculated (1·685 V) for the 1 M $HClO_4$ medium agreed very well with the value measured in this medium (1·66 V).

The relatively lower values of formal redox potentials in hydrochloric acid and phosphoric acid, and the decrease of these values with the increasing concentration of the acid is probably caused by the formation of tetravalent lead complexes with the anions of these acids[23].

Absorption spectra measurements

We have studied the absorption spectra of lead tetraacetate and diacetate in the ultraviolet region in media of the acids mentioned[39] in an attempt to elucidate the formation of these complexes. Only such concentration ranges of the individual acids could be selected for the measurement, in which the highly diluted lead(IV) salt solutions are sufficiently stable. The solutions were: 11 M $HClO_4$, 2–3·5 M H_3PO_4 and 0·1 N to 3·5 N HCl. The conclusions from these measurements may be summarized thus: spectra in a medium of glacial acetic acid differ from spectra measured in media of other mineral acids. In the first case the spectra show a rather indistinct peak at 280 nm, in the other cases the spectra show a clear peak. A substantial difference has been found in the stability of lead tetraacetate solutions. It has been confirmed from the analytical point of view that in glacial acetic acid lead tetraacetate solutions are very stable, especially if kept in the dark. According to the literature an explanation of this fact might be found in solvatation of lead tetraacetate molecules by acetic acid molecules. Strong illumination, especially ultraviolet radiation decreases this stability, a fact which may be ascribed to the formation of the acetoxy radical and its degradation into carbon dioxide and ethane.

Another unexplained point is the influence of the possible formation of tetravalent lead complexes in glacial acetic acid medium. From the data available in literature it follows that the presence of anionic as well as cationic complexes has been proved by electrophoretic means, in the presence of alkaline metal acetates mainly anionic complexes of the type $[Pb(CH_3COO)_5]^-$ or $[Pb(CH_3COO)_6]^{2-}$ have been found.

Measurements in 11 M $HClO_4$ have shown, that the absorption spectra of lead(IV) and lead(II) salts have peaks at approximately the same values, but the width of the absorption bands differ. Considering the high formal redox potential of the system Pb^{IV}/Pb^{II} in a medium of this acid (see preceding paragraph) as well as the fact that perchloric acid and perchlorates are not distinguished by complex-forming properties, it may be assumed that in this medium tetravalent lead will be present mainly in the ionic form. Lead tetraacetate solutions in media of perchloric acid are relatively less stable when exposed to light (compared, for example, with a medium of acetic acid), which may probably be attributed—with respect to the high formal redox potential—to the oxidation of water molecules by this reagent under the catalytic influence of light. In phosphoric acid solutions the absorption peak shifts with concentration variations of the acid, probably due to the formation of phosphate complexes of tetravalent lead. These complexes, whose composition is not yet known, cause stabilization of tetravalent lead solutions, since even in very dilute phosphoric acid solutions (down to 0·7 M H_3PO_4) they do not hydrolyse.

The most interesting results have been obtained from measurements in hydrochloric acid solutions. It has been proved that in solutions containing more than 0·7 N HCl lead tetraacetate converts quantitatively into the hexachlorolead(IV) anion $[PbCl_6]^{2-}$ and then decomposes, liberating chlorine due to a reaction with chloride ions

$$Pb^{IV} + 2Cl^- \rightarrow Pb^{II} + Cl_2$$

Based on the experiments performed, and the results obtained, it is impossible to decide unambiguously in which manner the oxidative effect of lead tetraacetate is manifested, e.g. in titrations of inorganic systems in hydrochloric acid medium or in the presence of chlorides, i.e. whether oxidation takes place by the effect of as yet unchanged lead tetraacetate molecules, or of tetravalent lead acetate complexes, or by the effect of the hexachlorolead complex, since the rate constants of oxidation by the individual systems, and of the conversion of lead tetraacetate into the hexachloroplumbate are not known.

Polarographic investigations

For a closer characterization of lead tetraacetate solutions, and to confirm the formation of the chloro-complex and liberation of free chlorine we have carried out a polarographic study of this reagent in perchloric acid and in hydrochloric acid media at such acid concentrations, in which lead tetraacetate is sufficiently stable. With regard to the high redox potential of the system Pb^{IV}/Pb^{II} we used a rotating platinum indicating electrode, polarized at + 2·0 V each time before recording the curve proper: curves were recorded up to + 0·4V. (Details of the preparation and maintenance of the electrode will be found in the respective communication[40]). In 11 M $HClO_4$ media we obtained well-developed and reproducible waves of tetravalent lead, corresponding to the reduction of $Pb^{IV} \rightarrow Pb^{II}$; the value of the half-wave potential is around 1 V. The wave-height is proportional to the tetravalent lead concentration in the range of 1×10^{-4} M to 3×10^{-3} M Pb^{IV} with a precision of ± 3 per cent.

In the range of attainable potentials (up to 2 V) bivalent lead compounds are not manifested in this medium. The tetravalent lead wave may be used for purposes of polarographic analysis, its limiting current (between 0·3 V and 0·7 V) may also be utilized for amperometric titrations with lead tetraacetate. In hydrochloric acid medium we have attempted a polarographic resolution of the chloroplumbate complex formed from the free chlorine, liberated only after a certain time (as already stated). It has been found that the waves can be reproduced in a medium of hydrochloric acid, i.e. chlorine may be distinguished from the chloroplumbate complex only when a rotating platinum electrode is used which has already been verified as indicating electrode on a series of curves recorded in perchloric acid medium[40]. In hydrochloric acid medium a wave appears after addition of a lead tetraacetate solution and polarographic recording, corresponding to the reduction Pb^{IV}/Pb^{II}. The height of this wave decreases with time, but its half-wave potential does not vary. A new wave appears at a more positive potential beside the original one, its height increasing with time. The identity of both waves has been confirmed by comparison, after addition of free chlorine, to a solution of hydrochloric acid or of lead tetraacetate. These results have been obtained in the range of 0·6 to 5 N HCl. The sharp decrease of the Pb^{IV} wave (whose rate increases with the increasing concentration of the acid) practically stops after some 15 min, whereas the chlorine wave decreases after several minutes more rapidly, due to volatilization of the element from the solution. The value of the half-wave potential of Pb^{IV} increased in solutions of 0·3 to 5 N HCl from 0·45 to 0·58 V. In solutions containing 5×10^{-5} M–1×10^{-3} M Pb^{IV} the dependence of the height of the polarographic wave in other words of limiting current values on the concentration of Pb^{IV} is linear in media of 0·6 N to 5·0 N HCl. It is possible to determine the Pb^{IV} content in this solution, as long as no more than a five-fold chlorine excess is present.

The polarographic study of lead tetraacetate in media of other mineral acids gave no reproducible results; the waves obtained were either not proportional to the Pb^{IV} concentration (in sulphuric acid solutions), or they included large peaks. In phosphoric acid media no polarographic wave was observed only a current rise from the zero line of the galvanometer upward was noticed; this was the case in glacial acetic acid also.

We have utilized the results obtained in the polarographic study of lead tetraacetate and in the study of its spectra to attempt a solution of the equilibrium of the Pb^{IV}/Pb^{II} system in hydrochloric acid medium, and we have investigated—based on the polarographic determination of the concentration of tetravalent lead in the presence of chlorine—variations of the equilibrium constant

$$K' = \frac{[Pb^{II}] \cdot [Cl_2]}{[Pb^{IV}]}$$

in dependence on the acidity of the solution. These results are described in detail in our original report[41], in the conclusion to which the possible scheme of the equilibrium is discussed based on the invariance of constants obtained for the system described in the range of 2 to 4·5 N HCl.

Utilization of lead tetraacetate as volumetric reagent

As to the analytical utilization of lead tetraacetate as volumetric reagent for the determination of inorganic and organic substances, a review of the applications is given in *Table 2*, together with the necessary explications in the text in the following paragraphs. Details are given in the original studies cited in the reference list.

Determination of inorganic substances

Among inorganic systems, titrated by direct potentiometric titration in solutions of sulphuric or hydrochloric acid, let us mention the determination of arsenic(III), antimony(III), tin(II), iron(II), titanium(III), chromium (II), thallium(I), molybdenum(III), ruthenium(IV), uranium(III), europium(II), salts, peroxidic substances, iodides, bromides, ferrocyanide, hydrazine, nitrite and thiosulphate[13, 14, 16, 19–21, 29].

All the titrations are rapid and precise, suitable for microdeterminations. Titrations of arsenic(III) salts diluted down to 10^{-5} M are possible with amperometric indication of the end point[35]. A new method of calculating the point of equivalence for amperometric titrations has been proposed for oxidation–reduction reactions, in which one of the reaction products is a low-solubility precipitate[35].

Thallous salts may be titrated even in amounts corresponding to 10 μg Tl; the method is very precise and is suited especially to the standardization of highly diluted lead tetraacetate volumetric solutions[19]. The high oxidation capacity of lead tetraacetate is proved by the fact that tetravalent ruthenium compounds may be oxidized directly to ruthenium(IV) oxide; the method is suitable for the determination of down to 2 mg Ru in a volume of 50 ml, the accuracy of the determination being equal to that of the gravimetric one. The method has been used to study the stability of different valency degrees of ruthenium compounds and to study the oxidation–reduction reactions to this element[21]. For microtitrations of trivalent and tetravalent uranium the method found suitable is that in which the sample is oxidized by an excess of ferric salt and the ferrous ions formed are titrated by lead tetraacetate; down to 20 μg U may thus be determined[24]. In the study of oxidation–reduction reactions of molybdenum we have found that in a medium of 10 N HCl compounds of trivalent molybdenum are oxidized to pentavalent molybdenum compounds, while in solutions of 5 to 7 N HCl the same oxidation by lead tetraacetate proceeds up to molybdates[19].

Reactions of lead tetraacetate with nitrites or peroxidic substances proceed rather slowly in acetic acid solutions. In the presence of chlorides (in the case of nitrites[29]) or of sulphates (in the case of peroxidic substances[44]) it is possible to bind the lead(II) salt being formed in a compound of low-solubility, shifting thus the reaction equilibrium in the required direction, so that the reaction is suitable for a reliable potentiometric determination. Thus it is possible, for example, to determine down to 0·5 per cent NO_2^- in soda saltpetre[29] or to determine the peroxidic component of hydrogen peroxide, magnesium, sodium, percarbonate, perborate, organic peroxides, etc. The reaction has been applied to the indirect, rapid microdetermination of uranium, after separating it in the form of a peroxo-compound, and the course of the unusual potentiometric curves has been explained[44]. In the titration of thiosulphates oxidation may proceed, depending on the reaction conditions, up to tetrathionates or sulphates[45].

The influence of the formation of low-soluble products on the shift of the reaction equilibrium, or on the increase of the oxidation effect of lead(IV) salts is clearly evident in the titration of iodides. With potentiometric indication e.g. in acetic or sulphuric acid medium the first potential change corresponds to the oxidation $2I^- \longrightarrow I_2$, the next potential change then indicates quantitative completion of the oxidation to iodate, a precipitate of lead(II) iodate being formed[46]. With regard to the reaction of bromides with lead tetraacetate, their oxidation to elementary bromine[46] may be utilized for analytical purposes. The titration of iodides as well as of bromides belong to the most sensitive methods of the volumetric determination of these halides. A study of the influence of the medium (type of acid), acidity, etc. on the titration has led to the possibility of determining, for example, iodides (in acetic acid medium) in the presence of an excess of bromides and chlorides. The method also is very well suited to the determination of the iodide component, e.g. in salts of organic quaternary bases[46].

In one of the most recent studies we have investigated the possibility of oxidizing europium(II) salts[34] and ferrocyanide[47]; both reactions are suitable for volumetric determinations, and especially the precision of the ferrocyanide determination is such, that we recommend this method for determining the titre value of lead tetraacetate solutions. Accurate results, however, may be obtained only in a medium of 0·5 to 5 N HCl, while at lower chloride ion concentrations, or in the absence of these ions, and in the medium of acetic acid (alone), phosphoric or perchloric acid, results are even 100 per cent higher. These errors occurred also in titrations of other systems, in which one-electron reactions took place (the oxidation of the ion determined). From our experiments and considerations it follows that in a medium containing a sufficient amount of chloride ions, the lead(IV) salt, i.e. lead tetraacetate is active in the form of the chloro-complex, whose oxidation effect is less energetic than, for instance, that of lead(IV) salts in a medium, in which they may be supposed to exist in the ionic form (e.g. in perchloric acid) in which the formal redox potential also attains the highest values (see preceding text). We assume, in agreement with some literature data, that in such a case the concern is with a bimolecular reaction between the ions determined and tetravalent lead, an active complex of formally trivalent lead being formed in the first stage, which is then reduced to the divalent state. In this process tetravalent lead may react with acetic acid (oxidation to CO_2). Details of this reaction are given in the original report[47].

Determination of organic substances

The determination of hydrazine and its derivatives (phenylhydrazine chloride, *p*-nitrophenylhydrazine, isonicotinic acid hydrazide, semicarbazide chloride) proceeds in the same way as with the use of other oxidants[36], the titration of a known amount of standard hydrazine sulphate solution is, due to its precision, suitable for determining the titre value of lead tetraacetate.

The reaction of hydroquinone, pyrocatechol and ascorbic acid[12] also proceeds in a highly satisfactory manner; the compound last-named may be titrated in glacial acetic acid, using N-N'-bis-4-(4-methoxyphenylamine)-phenyl thiourea as indicator[12a]. For many substances containing the sulphydryl group glacial acetic acid is a very good solvent, in which these substances are easily titrated with lead tetraacetate solution, generally with potentiometric indication[25], in some cases benzylmercaptan using quinalizarin as indicator[12]. In the non-aqueous medium of glacial acetic acid the oxidation of these compounds proceeds to the respective disulphides, while in a medium of dilute acetic acid, or in the presence of mineral acids, a substantial difference is observed in the oxidation products, e.g. thioglycollic acid is converted by an excess of the reagent in dilute acetic acid to the respective sulphinic acid, in the presence of hydrochloric acid to the sulphochloride. The oxidation of cysteine, thiourea and thiosemicarbazide[25] and of a number of organic sulphides (di-*n*-butylsulphide, di-*sec*-butylsulphide, *tert*-butyl-*sec*-butylsulphide, *tert*-butyl-*n*-butylsulphide, di-*tert*-butylsulphide, *tert*-butyl-isobutyl sulphide, *n*-butylphenyl sulphide, diphenyl sulphide and dibenzyl sulphide) has been studied in a similar manner.

Potentiometric titration in acetic acid medium may also be used for 1,4-anhydroerythrol, methyl-α-D-mannofuranoside, 1,4-anhydromannitol and methyl-2,6-anhydro-α-D-altropyranoside[17], and beside the platinum indicating electrode it is recommended to use for these cases a lead electrode.

As already stated in the introduction, the oxidation of organic compounds with a glycollic bond is one of the typical reactions of lead tetraacetate, differing from previous studies, in which the possibility of carrying out these reactions has been considered in non-aqueous media only. We have found that this reaction may also be performed in an aqueous medium (up to 50 per cent acid) or also that it may be greatly speeded by the presence of potassium acetate. This allows the determination of a number of substances, either by direct potentiometric titration (mandelic acid, tartaric acid, mannitol[16]) or by means of an excess of the reagent, its non-reacted amount being titrated by, for example, a hydroquinone volumetric solution. It is also possible to determine the equivalent amount of lead(II) salt, formed in the reaction, complexometrically[39]. This method has been used for the determination or study of the reactivity of formic acid[26], tartric acid[18], ethylene glycol, glycerine, mannitol, gluconate, mandelic, malic and citric acid with lead tetraacetate[22]. Details of the reaction mechanism in the oxidation of the compounds mentioned are given in the original papers[16, 22]. The developed analytical procedures have been applied, for instance, to the determination of glycerine in pharmaceuticals[27] and to determine the tartrate component of complex compounds[31].

Recently we have reported the possibility of determining the iodine number, in other words the double bond, using lead tetraacetate as volumetric reagent to generate bromine *in situ* from bromide added in excess to the sample dissolved in acetic acid (with addition of mineral acid, if necessary). This procedure brings several advantages, compared to methods in which for example bromine in glacial acetic acid is used as reagent for determining the iodine number: (*i*) lead tetraacetate is a very stable reagent, (*ii*) glacial acetic acid is a suitable solvent e.g. for a number of organic substances, (*iii*) the determination may be carried out by direct potentiometric titration. We have determined in this way diallylbarbituric acid, allylisopropylbarbituric, crotonic, oleic, erucic acid and determined the iodine number of rape, olive and ricinic oils. The method proposed may be used in the same way for substitution reactions, as we have proved by determining salicylic acid[49].

References

[1] C. R. Jacquelain. *Trav. Chim.* **7**, 1 (1851).
[2] O. Dimroth and F. Frister. *Ber. dt. chem. Ges.* **55**, 1231 (1922).
[3] O. Dimroth and R. Schweitzer. *Ber. dt. chem. Ges.* **56**, 1376 (1923).
[4] R. Criegee. *Ber. dt. chem. Ges.* **64**, 260 (1931).
[5] R. Criegee, L. Kraft and B. Rank. *Liebigs Ann.* **507**, 159 (1933)
[6] R. Criegee. *Chem. Zbl.* **11**, 2515 (1934).
[7] R. Criegee. *Angew. Chem.* **50**, 153 (1937).
[8] R. Criegee and E. Büchhner. *Ber. dt. chem. Ges.* **73**, 563 (1940).
[9] R. Criegee, E. Büchner and W. Werner. *Ber. dt. chem. Ges.* **73**, 571 (1940).
[10] R. Criegee. *Ber. dt. chem. Ges.* **68**, 665 (1935).
[11] P. Fleury and J. Courtois. *Inst. Intern. Chim. Solvay, Conseil Chim.* (R. Stoops, Bruxelles) 2279 (1950).
[12] O. Tomíček and J. Valcha. *Chem. listy* **44**, 283 (1950), *Coll. Czech. Chem. Commun.* **16**, 113 (1951).
[12a] L. Erdey, T. Meisel and G. Rady. *Acta. chim. Acad. Sci. Hung.* **26**, 71 (1961).
[13] A. Berka and J. Zýka. *Chem. listy* **52**, 926 (1958); *Coll. Czech. Chem. Commun.* **24**, 105 (1959).
[14] A. Berka, V. Dvořák, I. Němec and J. Zýka. *Analyt. Chim. Acta* **23**, 380 (1960).
[15] A. Berka. *Česk. Farm.* **8**, 561 (1959).
[16] A. Berka and J. Zýka. *Chem. listy* **52**, 930 (1958); *Coll. Czech. Chem. Commun.* **23**, 2005 (1958).
[17] R. E. Reeves. *Analyt. Chem.* **21**, 751 (1949).
[18] A. Berka. *Analyt. Chim. Acta* **24**, 171 (1961).
[19] A. Berka, J. Doležal, I. Němec and J. Zýka. *Analyt. Chim. Acta* **25** 533 (1961).
[20] A. Berka, J. Doležal, I. Němec and J. Zýka. *J. Electroanalyt. Chem.* **3**, 278 (1962).
[21] I. Němec, A. Berka and J. Zýka. *Mikrochem. J.* **6**, 525 (1962).
[22] A. Berka, V. Dvořák and J. Zýka. *Mikrochim. Acta.* 541 (1962).
[22a] J. Zýka and A. Berka. *Mikrochem. J.*, Symp. Series, Vol. 2, 789 (1962).
[23] A. Berka, V. Dvořák, I. Němec and J. Zýka. *J. Electroanalyt. Chem.* **4**, 150 (1962).
[23a] A. Berka, J. Janata and J. Zýka. *Coll. Czech. Chem. Commun.* **29**, 2242 (1964).
[24] A. Berka, J. Doležal, I. Němec and J. Zýka. *Analyt. Chim. Acta* **26**, 148 (1962).
[25] L. Suchomelová and J. Zýka. *J. Electroanalyt. Chem.* **5**, 57 (1963).
[26] A. S. Perlin. *Analyt. Chem.* **26**, 1053 (1954).
[27] A. Berka, M. Fara and J. Zýka. *Česk. farm.* **12**, 366 (1963).
[28] G. Frisona and S. King. *Analyt. Chem.* **34**, 40A (1962).
[29] A. Morales and J. Zýka. *Coll. Czech. Chem. Commun.* **27**, 1029 (1962).
[30] A. Berka. *Z. Analyt. Chem.* **195**, 263 (1963).
[31] J. Loub and V. Frei. *Chem. Zvesti* **16**, 802 (1962).
[32] J. Zýka and A. Berka. Proceedings "Feigl Anniversary Symposium" Birmingham 1962, p. 383.
[33] J. Zýka. *Rudy* **12**, 177 (1964).
[34] V. Tolar, I. Němec and J. Zýka. *Zhur. Anal. Khim.*, in print.
[35] J. Adámek, J. Doležal and J. Zýka. *Microchem. J.* **8**, 1 (1961).
[35a] J. Adámek, J. Doležal and J. Zýka. *Coll. Czech. Chem. Commun.* **28**, 2131 (1963).
[36] A. Berka, J. Vulterin and J. Zýka. *Selected oxidation–reduction volumetric methods, in Czech* (State Publishing House of Technical Literature, Prague), 1961.
[37] A. Berka, J. Vulterin and J. Zýka. *Massanalytische Oxidations und Reduktionsmethoden* (Akad. Verlagsges. Geest u. Protig, Leipzig), 1964.
[38] A. Berka, J. Vulterin and J. Zýka. *Newer Redox Titrants* (Pergamon Press, Oxford), 1965.
[39] I. Němec, V. Dvořák and J. Zýka. *Microchem. J.* **11**, 153 (1966).
[40] I. Němec, V. Dvořák and J. Zýka. *Microchem. J.* **11**, 172 (1966).
[41] I. Němec, V. Dvořak and J. Zýka. *Microchem. J.* **11**, 183 (1966).
[42] W. M. Latimer. *The oxidation states of the elements and their potentials in Aqueous Solutions* (Prentice Hall, New York), 1952.

[43] G. Charlot. *Oxidation–reduction Potentials* (Pergamon Press, London), 1958.
[44] O. Borecký and J. Zýka. Unpublished results.
[45] E. Rencová and J. Zýka. Unpublished results.
[46] V. Buzková, B. Moldán and J. Zýka. *Coll. Czech. Chem. Commun.* **30**, 28 (1965).
[47] V. Tolar, I. Němec and J. Zýka. *Zhur. Anal. Khim.*, in the press.
[48] L. Suchomelová, V. Horák and J. Zýka. *Microchem. J.* **9**, 201 (1965).
[49] A. Berka, K. Sigler and J. Zýka. *Microchem. J.* **11**, 398 (1966).