SPECTROPHOTOMETRIC DETERMINATION OF MINUTE LEAD CONTENTS OF NATURAL AND INDUSTRIAL OBJECTS

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Lead is one of the most toxic biologically active elements. Because it ranks first among microelements as regards atmospheric deposition, it is important to develop direct rapid methods for controlling the lead content of various natural and industrial objects.

Many publications are available on the analytical chemistry of lead, but state-of-the-art reviews are rare; the most recent reports appeared in 1972–1981 /1-7/. We have attempted to assess a number of new methods of determining minute amounts of lead from the standpoint of their application in the operational testing of lead content in environmental objects.

The main methods of determining minute concentrations of lead include: atomic absorption spectrometry, neutron activation analysis, atomic emission spectrometry, electrochemical and photometric methods.

The last decades have seen wide use of physical methods: atomic absorption spectrometry /8-14/, atomic emission spectrometry /15-17/, neutron activation /18, 19/ and mass spectral /20, 22/ analyses, which are highly sensitive and require complex equipment; they are employed to analyze alloys, steel, rock ores, soil extracts, water and industrial effluents, aqueous and atmospheric suspensions that contain lead.

Of all the above mentioned physical methods of analyses, the most promising and intensively developed method which provides high sensitivity, speed and accuracy, is certainly atomic absorption spectral analysis. However, despite the constant perfection of the method, the analysis of natural objects with complex composition presents certain difficulties. With the complication of the qualitative composition of the analyzed subject and an increase in sample size, the influence of the matrix on microimpurity determination grows. There is not yet a clear idea of the physico-chemical processes taking place in atomizers, and the actual reasons for a change in the analytical signal in the presence of accompanying elements have not been revealed. Ways to eliminate this influence are still to be found. There is a lack of reliable, electrothermal atomic absorption methods of determining lead in rocks, waters, ores, and refined products, which would secure the required limit of detection. Therefore, the sensitivity of the direct atomic absorption determination constitutes $10^{-2}-10^{-4}$ % for solid samples, and $10^{-4}-10^{-6}$ % for aqueous solutions /12/.

Known electrochemical methods for lead determination, *viz.* polarographic /23-26/, potentiometric /27-29/, amperometric /30, 31/, electrogravimetric /32-37/, coulometric /38-42/, are seldom fully adequate. Of great interest is lead determination in alloys, semiconductor and reactor materials. Most of the electrochemical methods described exhibit low reproducibility, require complex and expensive equipment, are characterized by long duration of the analysis, and lack sufficient selectivity for lead determination in the presence of other elements. In fact, the only way to increase selectivity is to combine these and other separation and concentration methods such as extraction, chromatography and coprecipitation.

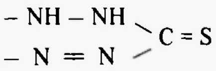
A number of modifications of gravimetric /43-45/ and titrimetric /46-48/ lead determination methods have been developed for lead in iron, copper and polymetallic ores, halenite and silicate rocks; however, they are time-consuming and insufficiently sensitive.

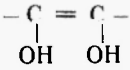
Despite the new promising methods of physical analysis, laboratories of analytical chemical testing still prefer photometric methods with organic reagents which are certainly advantageous in terms of simple equipment, available reagents, instruments, wide range of determinable concentrations (from 10^{-4} % to 100%), accuracy and sensitivity.

The published data indicate that over the last few years organic reagents have moved to the centerspot in the analytical chemistry of lead. However, all the known colour reactions of lead with the use of these reagents are insufficiently selective. Therefore, the search for new reagents as well as the selection of new conditions for application of the old ones are important for chemical analysis.

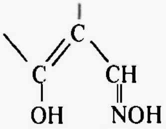
In the present review we shall try to present a comparative analysis of photometric and extraction photometric methods of lead determination that appeared over the last 15 years, with the purpose of making the correct choice of methods depending on the object and conditions of the analysis.

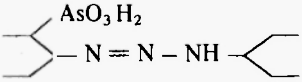
It is known that various classes of organic reagents with the following functional analytical groups present in their molecules interact with lead /49/:

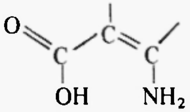


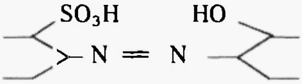


$$-\underset{\textstyle OH}{\underset{|}{C}}=\underset{\textstyle OH}{\underset{|}{C}}-$$



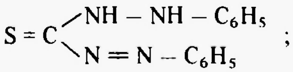






These groups, however, can react also with copper, zinc, cadmium, mercury, cobalt, nickel, and other elements.

Dithizone has the greatest practical application:



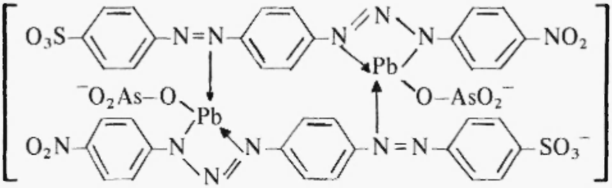
and is widely used for lead determination in biomaterials /50, 51/, soils and silicate rocks /52-54/, waters /55, 56/, air /57/, metals and alloys /58, 59/.

Dithizone is considered to interact with lead at pH 8.0–10.0 in enolic form to produce $Pb(HDz)_2$ /60/. The structure of complexes formed by the dithizone enol tautomer is still to be solved and demands further study /61/. The reaction is highly sensitive. Its drawback is low selectivity. Manganese, nickel, copper, zinc, cadmium, bismuth, mercury, silver, and other elements interfere with the determination. Moreover, the reagent is poorly water-soluble, unstable in acidic media and decomposes under the influence of light. Selectivity can be improved by either the preliminary extraction of the lead chloroform complex, or the introduction of cyanide as masking agent.

To determine lead in solid particles of industrial facilities /62/, natural waters, biological objects and salts /63-70/, sulfarsazene is used (4”-nitrobenzene-1”, 4-diazo-amino-1,1-azobenzene-2”-arsono-4-sulfoacids). While it is less sensitive than dithizone, it has a number of advantages: it is water-soluble, easy to handle and needs no cyanide as masking agent. But, it has insufficient reaction selectivity. Manganese, nickel, copper, zinc, mercury, cadmium, iron, zirconium, and other elements interfere with the determination. The methods developed on the basis of sulfarsazene require a preliminary ion separation; for instance, lead is separated by extracting with dithizone solution in carbon tetrachloride /71/, which is time-consuming.

Study of the reaction of sulfarsazene with lead ions /72, 73/ points to simultaneous participation of the lead cation with triazene and arson groups in complex formation.

Polarographic investigation /74/ confirmed the existence of lead bonds with the o-arsonotriazene group of the reagent, and cleared up the azo-group contribution to the formation of the complex which may be due to coordinative bonding with lead atoms. The role of the nitrogroup as an electrophilic substituent that improves the mobility of the hydrogen atom of the aminogroup was experimentally confirmed. The structure of the resultant compound is as follows:



Arsazene (4''-nitro-2''-arsonobenzene-1'',4-diazoamino-1,1-azobenzene) is a sulfarsazene analogue, different in that it lacks a sulfogroup, which makes its lead products extractable by some organic solvents /75/. Arsazene is practically as sensitive as dithizone. Manganese, nickel, copper, zinc, mercury, cadmium, iron, lanthanum, tin, and other elements interfere with the determination. Arsazene makes it possible to determine 0.5 μg of lead in volumes of up to 500 ml, while the sensitivity of sulfarsazene is 0.5 μg of lead in 5 ml solution. Nevertheless, because of low selectivity and restricted range of possible objects of analysis, the photometric determination of lead with arsazene is rarely used.

Inorganic reagents are seldom used in photometric lead determination since they are poorly sensitive and solutions of their complexes are generally insufficiently stable. The only inorganic reagent sometimes used for photometric lead determination is potassium iodide that forms a complex ion, $[PbI_4]^{2-}$ with lead. Zinc, cadmium, cobalt, nickel, manganese, copper, tin, and other ions interfere /76, 77/.

Hydrorubeanic acid (dithiooxamide) was suggested /78/ as an analytical reagent for lead determination in bronze and brass. Interference of copper, silver, bismuth, mercury, cobalt, nickel, cadmium ions, is eliminated with electrolysis. The sensitivity of the method is 10 μg/ml. Due to the insufficient sensitivity and selectivity the method is seldom used in analytical laboratories.

Lead rubeante solubility is explained by its reaction with OH ions:

$$PbC_2S_2N_2H_2 + n\overline{OH} = [Pb(OH)_n^{C_2S_2N_2H_2}]$$

The exact structural formula of the complex was not determined.

Of the indirect photometric lead determination methods, that based on the use of diethyldithiocarbamate /79-81/, which forms a colorless lead complex in an alkaline medium, is most widely used. The complex can be extracted with chloroform and carbon tetrachloride. Lead is quantitatively replaced from extracts by copper ions that form a colored complex. The range of the determinable concentrations is 0.005–0.5% of lead. The time of analysis is 2–3 hours. The method is insufficiently sensitive and poorly selective. To eliminate the interference of copper, iron, nickel, cobalt, manganese and zinc ions, lead is either extracted from ammonium citrate medium with the addition of potassium cyanide solution /81/ or the interfering ions are preliminarily removed in the form of pyridine –CNS complexes by extracting with chloroform /80/. All the reagents undergo special purification. The method is used for lead determination in extrapure reagents.

Paper /82/ describes a technique for the indirect determination of 10–50 μg of lead based on a decrease in absorbance of the trioxyglutarate – Fe(III) solution resulting from the formation of the complex of Fe-Pb-trioxyglutaric acid in the pH range 4.0–10.0. Cadmium, zinc, copper, nickel, and cobalt interfere.

Among a large group of hydroxyl-containing photometric reagents, representatives of the following classes of compounds have been chosen: sulfophthaleines /83-95/, oxyanthraquinones /96-99/, oxyazo compounds /84, 100-112/.

Let us examine these compounds more closely.

Among organic reagents for photometric lead determination a group of compounds of the triphenylmethane series is most interesting: catechol violet (CV), xylenol orange (XO), methyl thymol blue (MTB), glycine thymol blue (GTB), and bromopyrogallol red (BPR), a xanthene derivative.

CV reacts with lead in ammonium buffer, yielding the complex Pb:R ~ 1:1 /85, 86/. An increased lead concentration gradually leads to a complex with a 2:1 ~ Pb:R ratio, which is less stable. The addition of gelatin leads to the formation of the complex Pb:R ~ 1:2.

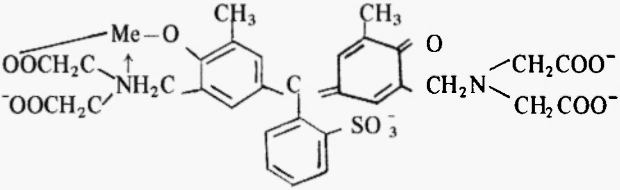
The conditions of complex formation of lead with XO have been studied by a number of authors /87-90, 84/. However, the spectrophotometric characteristics of this complex described in the papers are conflicting. There is no unanimous opinion about the composition of the complex formed; different pH values and molar extinction coefficients are presented.

XO was proposed for lead determination in water after a preliminary extraction with dithizone and subsequent re-extraction /84/. The method is poorly selective being handicapped by copper, nickel, cobalt, zinc, bismuth, iron, aluminium, which therefore requires an additional labour-consuming separation of lead from interfering elements. Insufficient stability of aqueous solutions of the reagent also limits its use.

The determination of lead by methods based on the use of MTB were also developed. The reaction is insufficiently sensitive. The Beer law is valid in the 0.4–8 μg/ml concentration range /84, 91-94/.

Of the remaining reagents of the triphenylmethane series, complex formation of lead has been studied for bromopyrogallol red /95, 113/, glycinethymol blue /83, 84/ and glycinethymol glycinecresol red /78/.

Despite a great number of papers on complex formation of XO and MTB with metals, there is no unanimous opinion on the reaction mechanism. The formation of chelates is explained /88, 114, 115/ by the appearance of two ionic bonds between the metal and carboxylic and phenol oxygen, and a donor-acceptor bond with the nitrogen of the iminodiacetate group:



For instance, some authors /116-117/ believe that complexes with a Pb:R ratio 1:1 are actually dimers. Paper /118/ suggests the existence of an ionic bond between metal and the oxygen of the phenol group and a coordinative bond with nitrogen; the possibility of complex formation *via* the carboxylic groups is ruled out completely.

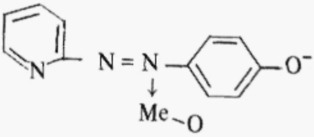
According to the literature data, sulfophthaleines in a neutral medium form lead complexes with low molar extinction coefficients. The formation of extractable ionic lead associates with triphenylmethane reagents and diphenylguanidine /87-89/ does not improve the spectrophotometric characteristics of the complexes. It is possible to increase the sensitivity of the lead determination slightly using ionic associates of lead with 1,10-phenanthroline and sulfophthalic ions that are extracted with chloroform at $2.3 \times 10^3 - 3.5^7 \times 10^4$-fold excess of 1,10-phenanthroline /119/.

Azo compounds based on chromotropic acid and o-aminophenylarsonium acid, particularly arsenazo III, are also of some interest for photometric determination of lead /101-103/, but the methods are insufficiently sensitive. Bismuth, copper, iron, and tin hinder the determination of lead with arsenazo III.

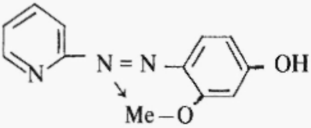
Thus, on the basis of the literature data, we can make the following conclusions. Complexes of lead with oxyazocompounds not containing a heteroatom in the diazo component have low molar extinction coefficients /84, 101/ and poor stability. The stability constant of lead complexes with arsenazo III is 2.9×10^5 /102/, with carboxyarsenazo 2.5×10^6, with rhodasole-XC, 2.9×10^3, and with magnesone-XC 1.2×10^8 /84/. The ratio of the components in the complexes is 1:1. Moreover, the reactions of lead with oxyazo compounds are poorly selective. The selectivity may be enhanced at the cost of slightly poorer limits of lead determination either by extracting multiligand lead complexes with oxyazo compounds and diphenylguanidine /84/, or by preliminary extraction of lead with a solution of ammonium hexamethylenethiocarbamate in chloroform /102/.

One of the more lead-sensitive reagents is 4-(2-pyridylazo)-resorcinol (PAR). The conditions of complex formation of lead with PAR were studied by several authors /84, 104-108/, but again contradictory data were reported. Thus, the authors of /106/ assumed the formation of two lead complexes with PAR: the first with a Pb:R ratio equal to 1:1 (pH 2.3–5.0; $\epsilon_K \sim 1.08 \times 10^4$), and the second with a Pb:R ratio equal to 1:2 (pH 5.0; $\epsilon_K \sim 5.0 \times 10^4$). Other works mention only one complex: Pb:R ~ 1:1 /104, 108, 84/, but cite various optimal pH values and molar extinction coefficients.

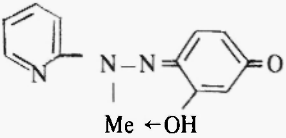
The chemistry of PAR interactions with metal ions is described in papers /120-122/. Most authors /123-125/ explain the formation of the complex by the participation of the hydroxyl group oxygen, pyridine nitrogen and azo group nitrogen which is farther from the pyridine ring:



The authors of /126/ describe PAR as an equilibrium system of azo- and quinonehydrazone forms and believe that a simultaneous coordination of the element with the azo group and nitrogen atom of the pyridine ring within a single molecule in hindered as the distance between the Me-O and Me-N bonds will become less than the sum of the ionic radii. This allows us to propose two possible structures for Me:R ~ 1:1 complexes with PAR.



azo form



quinonehydrazone form

PAR is not a selective reagent. Zinc, iron, copper, cobalt, cadmium, nickel, bismuth, molybdenum and other metals interfere. PAR has been proposed /127/ for the photometric determination of lead in steel, brass, and bronze. The method is based on preliminary extraction of numerous interfering ions with methylisobutylketone from their thiocyanate complexes, subsequent separation of lead by extracting its iodide complex with methylisobutylketone, reextraction from the organic phase to the water phase, and determination with PAR in the presence of cyanide.

The first data on lead interaction with PAR were obtained by the authors of /109/. They found that in the pH range 2 to 7 chelates are formed with a component ratio of 1:1. At pH 3–4, solutions with excess metal are believed to yield the formation of the protonated complex PbRH ($\epsilon_K \sim 1.97 \times 10^4$). In equimolecular solutions at pH 4–6 the formation of normal PbR chelate predominates (Me:R $\sim$ 1:1, $\epsilon_K \sim 3.0 \times 10^4$). In another work /106/, the same authors point out the formation of another lead complex with TAP in 0.5 M H_2SO_4 ($\epsilon_K \sim 8250$).

In /128/ an extraction photometric method of lead determination with thiodibenzoylmethane as a reagent is described. The analysis is time-consuming. The selectivity with respect to non-ferrous and transition metals is achieved by introducing cyanide as a masking agent.

Quinalizarin was also proposed as an organic reagent for determination of lead /98/. To improve solubility of lead quinalizarinate, it was proposed /99/ to use water-acetone media. Because of their low sensitivity and selectivity, however, /96, 97/ alizarin and quinalizarin are seldom used as analytical reagents for lead.

1,5-di-(benzylbenzimidazolyl)-3-methylformazan from the symmetric formazan class of the benzimidazole series was described as a new high-sensitivity reagent for the extractive photometric determination of microgram amounts of lead /129/. The reaction in water-acetone and chloroform media is highly sensitive. A conditional instability constant of the complex in a water-acetone medium of 3.93×10^{-17}, calculated with due regard for the formazan dissociation constant, points to high stability. To separate lead from interfering ions, the method of anion exchange in chloride solutions was used. The extractive photometric determination of lead was employed in the analysis of biological objects.

The authors of /130/ used an extractive photometric modification for determining lead (0.01–0.5%) with derivatives of dimercaptothiopyrone for the analysis of steel, cast iron, brass, and barite concentrators. A recently synthesized pyrazolone dye of the triphenylmethane series, *viz.* bis-(4-dimethylaminophenyl)-(1,3-divinyl-4-chloropyrazolone-5-yl)-carbinol, termed phenylpyrazolone green, was proposed for the photometric and extractive photometric determination of lead /131/. It was established that the formation of ionic associates between the metal halogenide (or metal rhodanide) anions and the cation of the reagent is accompanied by a change of the brown-red colour to bright green and subsequent precipitation. The precipitates are easily stabilized in the form of colloids or suspensions and are easily extracted with benzene. The reaction is not selective. For extractive photometric determination, only chloride and bromide systems are suitable.

Thus, it can be stated that photometric methods of lead determination in complex objects used in practice comprise a preliminary separation of interfering ions. For instance, the determination of lead in bronze with hydrorubeanic acid calls for electrolytic separation of interfering ions /78/; determination of lead in steel, cast iron, and other objects with dithizone involves adsorption on anion resin /127, 132/ or three extractive separation stages: 100% iron, 80% molybdenum and 70% tin is extracted with pentylacetate; then follows the extraction of diethyldithiocarbamate complexes of lead and bismuth from a cyanide medium; finally the dithizone complex of lead is extracted with chloroform /133/. When lead is determined in rock with dithizone, the influence of iron and zinc is eliminated by the extraction of their ions with ethylacetate in the form of rhodanide complexes /134/ or diethyl ester /135/.

The determination of lead in steel, brass and bronze with PAR involves separation of large amounts of copper in the form of an ammonium complex, followed by the extraction of thiocyanate complexes of other interfering ions and of the lead iodide complex with methylisobutylketone /104/.

In the method based on the use of sulfarsazene, iron is extracted with isoamyl alcohol in the form of its thiocyanate complexes /74/.

Organic reagents employed in the photometric determination of lead are given in Table 1. It should be noted that in many papers there are data neither on sensitivity /85, 86, 97, 106, 107, 118, 110, 127, 81, 141-146/ nor on selectivity of the reactions /84, 110-112, 100, 61, 127, 136-138, 87, 113, 141-146/. The authors only established the Me:R ratios and assumed the equations of complex formation of lead with organic reagents. In a number of papers /87, 106, 107, 100, 136, 127, 137, 95, 141-146/ there are no data on the composition of the complexes being formed.

As seen from Table 1, most organic reagents react with lead at pH 8–10. Values so high make determination of lead difficult due to hydrolysis of its ions which results in low selectivity and poor reproducibility of the determination.

To improve selectivity of photometric determination of lead, it is more promising to perform complex formation at lower pH values.

In this respect reagents based on thiopropirhodanide are of practical interest since they allow the direct determination of lead in more acidic media in the presence of non-ferrous, heavy, platinum, alkali, and alkali-earth metals. Tirodine [5-(2-hydroxy-3-sulfo-5-chloro-

TABLE 1

Comparative Characteristics of Organic Reagents for the Photometric Determination of Lead

Reagent	$pH_{opt.}$	Maximum absorption, $_{MeR}^{nm}$	Molar extinction coefficient, $n=\epsilon_{MeR}\cdot 10^{-4}$	Me:R ratio in the complex	Interfering elements	Ref.
1	2	3	4	5	6	7
1. Dithizone	8.0–10.0	520	6.6	1:1	Ni, Cu Hg, Ag Zn, Sn, Bi, Fe, Mn, Cd, Au etc.	/60/
2. Arsazene	10.0	485	6.4	1:1	Ni, Cu, Zn, Cd Hg, Fe, Sn Mn	/75, 136/
3. Sulfarsazene	9.0	500	4.5	1:1	Cu, Zn, Cd, Co Mn, Fe, Ni, etc.	/72–74/
4. Hydrorubeanic acid	12.0	540	0.1	1:2	Cu, Zn, Cd, Co, Mn, Fe, Ni, etc.	/78/
5. Sodium diethyldithiocarbamate copper	10.5–12.4	435	1.3	1:1	Bi, Cd, Tl, Pt, Pd, Au	/79–81/
6. Pyrocatechol violet (PV)	9.0–10.0 9.0–10.0	555 640	– –	1:1 1:2	Ti, Ga, Jn, W, Mn, Bi	/85, 86/
7. Xylenol orange (XO)	5.6–5.8 4.5–5.5 4.5–5.3	572 584 580	1.38 1.94 –	– 1:1 1:1 and 1:2	Cu, Ni, Co, Zn, Bi, Fe Fe, Al, Cd, Tl	/87, 88, 89, 90, 84/

TABLE 1 – Continued

1	2	3	4	5	6	7
XO – cont.	5.0–5.6	580	1.74	1:1		
	6.0	576	1.9	1:1		
	4.5–6.5	570	1.9	1:1		
8. Methyl thymol blue (MTB)	5.8–6.5	600	1.64	1:1	Al, Ni, Fe, Cu, Mn Zn Cr, Sn, Be, Th, Zr, Cd, Bi	/84, 91, 92,93,94/
9. Glycinethymol blue (GTB)	7.8	570	2.13	1:2	Al, Zn, Fe, Sn, Ni, Cu, Ti, Hf	/83, 84/
	6.6–7.2	560	0.92	1:2		
	8.0	590	0.8	1:2		
10. Bromopyrogallol red (BPR)	5.5	630	0.5	1:1	Cu, Th, La, Ce, Hf, Ni, Ti, Al, Fe	/95,113/
	9.0	610	0.8	1:2		
11. Alizarin	5.4–8.2	490	–	1:1	Zn, Mn, Ni	/96, 97/
12. Quinalizarin	6.2–8.2	533	0.5	1:1	Fe, Cr, Ni, Zn	/98, 99/
	6.2–6.4	533	0.5	1:1	Mn, W, Cu, Al	
13. Arsenazo III	4.0–5.0	665	1.0	1:1	Bi Cu, Fe, Sn	/103, 102/
	4.0	597, 660	2.77	1:1		
	4.0	605, 665	2.8	1:1		
14. Carboxyarsenazo (CA)	4.0–4.5	610–660	1.07	1:1		/84/
15. Magnezone-XC (MXC)	6.0–7.0	540	1.01	1:1		/84/

TABLE 1 – Continued

1	2	3	4	5	6	7
16. Rhodazol-XC (RXC)	7.0–7.5	500	0.76	1:1		/84/
	9.8–10.2	550	0.88	1:2		
17. 4-(2-pyridyl-azo)-resorcinol (PAR)	8.0–10.0	520	4.0	1:1	Cu, Fe, Zn, Co, Cd, Ni, U	/105, 106/
	10.0	530	–	–		
	2.3–5.0	512	1.08	1:1		/106/
	5.0	–	5.0	1:2		
	8.0–8.8	520–530	–	–		/107/
	6.0–10.0	515	–	1:1		/118/
	7.5–9.0	520	3.48	1:1		/84/
18. 4-(2-thiazolyl-azo)-resorcinol (TAR)	3.6–4.1	540	1.97	1:1	Cu, Bi, Ni, Zn, Co, Fe	/109/
	6.1–8.1	530	3.04	1:1		/106, 87/
	–	600	0.82	1:1		
19. 1-(pyridyl-azo)-2-naphthol (PAN)	6.0–10.0	533	–	1:2		/110/
	6.2–6.3	550	2.48	1:1		/111/
	–	570	2.02 and 1.49	1:1 and 1:2		/111/
	–	–	1.92	1:3		
	6.3–6.9	550	2.99	1:1		/111/
	–	570	2.06	1:1		
	–	–	1.9	1:3		
	–	575	1.76 and 1.06	1:1		/112/

TABLE 1 – Continued

1	2	3	4	5	6	7
PAN – cont.	6.5	555	1.45	1:1		
	–	–	0.903	1:2		
20. 2–(5-bromo–2–pyridyl–azo)–5–diethyl-aminophenol (Br–PAAP)	6.77	575	4.9	1:1	Cu, Mo, Ni, Fe	/100/
21. 2–(4–antipyryl–azo)–5-diethyl–amino-m–phenol (ANAP)	–	520	0.58	–		/100/
22. 2–(2–thiazolyl–azo)–5–diethyl-amino)–m-phenol (TAAP)	–	575	0.8	–		/100/
23. Tetraoxyquinoline	3.0	520	0.04	1:1	Cu, Hg, Co, Ni, Zn	/136/
24. Glycinecresol red	7.0	560	1.4	1:2	Cu, Zn, Ni, Co, Cd, Bi, Tl, Fe, Al	/78/
25. Malic acid	5.8	265	0.5	1:3		/61/
	10.0–11.0	305	0.5	1:3		
26. 8-hydroxy-quinoline	–	400	4.6	–		/136/

TABLE 1 – Continued

1	2	3	4	5	6	7
27. Sodium chloranilate	4.63	520–530	–	–		/127/
28. Potassium diethyldithiophosphate	–	295	7.7	–		/137/
29. Formazan	11.5–13.5	550	1.09	1:2		/138/
30. 7–[α–(o–carbomethoxyaniline) benzyl–8–hydroxyquinoline	10.0–13.0	390	0.45	1:1	Al, Zn, etc.	/139/
31. Na–diketohydrindilidene-diketohydrindiamine	4.5	560	3.97	1:2		/140/
32. Pyridyl-azo–monoethyl–aminoparacresol	8.0–9.0	530	5.3	1:1		/87/
33. Trioxyglutaric acid-Fe(III)	4.0–10.0	400	–	1:1:1	Cd, Zn, Cu, Ni, Co	/81/
34. 1,10 phenanthroline + eosin	6.5	550	1.1	1:2:1		/113/

TABLE 1 – Continued

1	2	3	4	5	6	7
35. Tetraphenylporphinetrisulfoacid	9.8–10.5	464	27.5	–	Cu, Cd, Fe, Hg	/95/
36. Diphenylcarbazone	–	535	6.13	–		/137/
37. Di-β-naphthylthiocarbazone	–	550	8.0	–		/137/
38. Eriochrome grey	7.7–8.0	540	–	–		/141/
39. Chlorophosphonazo–III	1.5	745	–	–		/142/
40. 7–(2–pyridyl–azo)–8–hydrooxyquinoline	3.0	560	–	–		/143, 119/
41. Gallein	4.4	560	–	–		/144/
42. Thiothenoyltrifluoroacetone	5.0	440	–	–		/145/
43. Fast blue	8.5	536	–	–		/146/
44. Tyrodine	3.0–5.0	590	4.2	1:2	Ag	/147/

phenylazo)-2,4-dithion-1,3-thiazane] was thus proposed as a sensitive and selective reagent for lead /147/. Lead reacts with the reagent at pH 2–6, yielding a stable complex. Nickel, cobalt, iron, zinc, gold, rhodium, platinum, lanthanum, beryllium, manganese, calcium, and other elements have practically no effect on the determination. Only silver interferes. Such a high reaction selectivity makes possible direct determination of lead in many objects, for example, in process water in the production of lead anodes and cathode copper during electrical melting, sulphuric acid, lead and lead molybdate chromes and cables, without preseparation of lead from accompanying elements. Rapidity of analysis as well as high sensitivity and reliability are attained.

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