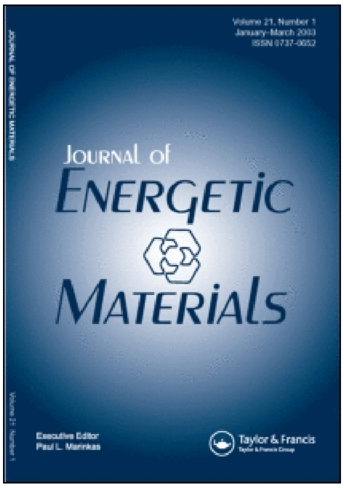

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DIFFERENTIAL PULSE POLAROGRAPHIC ANALYSIS OF LEAD NITRORESORCINATES

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ABSTRACT

A differential pulse polarographic method for analysing the lead and nitroresorcinate contents of lead-2-mononitroresorcinate, lead-2,4-dinitroresorcinate and lead-2,4,6-trinitroresorcinate-monohydrate is described. The analysis is based on the fact that in the presence of a complexing agent the polarographic reduction of the formed lead complex is displaced toward more negative potentials relative to free lead ions. In the presence of both NTA (nitrilotriacetic acid) and EDTA (ethylenediaminetetraacetic acid) the lead peak is completely separated from the peaks for the nitro-groups in the nitroresorcinates. The method can also be used for a qualitative and quantitative analysis of mixtures of two different lead nitroresorcinates. The lead nitroresorcinates that are difficult to dissolve can be completely dissolved in the presence of both NTA and EDTA.

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INTRODUCTION

The lead salts of resorcinol (1,3-benzenediole or 1,3-dihydroxybenzene) with nitro groups in 2-, 2,4- and 2,4,6-positions, namely lead-2-mononitroresorcinate, lead-2,4-dinitroresorcinate and lead-2,4,6-trinitroresorcinate-monohydrate are used as primary explosives and as components in ignition compositions.

Different methods can be used to analyse lead nitroresorcinates but the only method by which it is possible to simultaneously analyse both the lead and nitroresorcinate is polarography. Both lead ions and nitro groups are reduced at a dropping mercury electrode. In an 1 M ammonium acetate solution the reduction takes place within the same potential range and overlapping polarograms are obtained for lead and nitro groups. A differentiation of the polarograms is obtained by second harmonic AC polarography (1). The method is interesting but not particularly suitable for routine analyses. In this investigation it is shown how one can analyse the lead nitroresorcinate using differential pulse polarography by transferring lead ions with NTA (nitrilotriacetic acids) or EDTA (ethylenediaminetetraacetic acid) to a lead complex that is reduced at a considerably more negative potential than the nitro groups. The analysis of lead nitroresorcinate is, then, carried out as two independent single-component systems with completely separated differential pulse polarograms. The nitroresorcinate contents in mixtures of two different nitroresocinates are analysed as a two-component system with overlapping polarograms. The lead content can also in these cases be analysed quite independently of the nitroresorcinates.

The lead nitroresorcinates are relatively difficult to dissolve in pure water solutions and the solubility increases in the presence of a complexing agent, which is an advantage.

THE SOLUBILITY OF LEAD NITRORESORCINATES

Lead nitroresorcinates have a relatively low solubility in a pure water solution. The solubility for lead-2,4,6-trinitroresorcinate-monohydrate is given as pL = 6.1 (2). The solubility products for lead-2-mononitroresorcinate and lead-2,4-dinitroresorcinate are not known. The solubility increases with decreasing pH of the solution as a result of the reaction of the nitroresorcinates with hydrogen ions. Resorcinol is a very weak dibasic acid, i.e. it forms stable complexes with hydrogen ions. With electronattracting nitro groups in the aromatic ring the strength of the acid groups increases. The solubility of lead nitroresorcinates can also be raised by adding a complexing agent (=Y) to the solution, such as NTA or EDTA, which forms soluble complexes with lead ions.

The conditional solubility product (3) which gives the solubility in a certain solution is defined as:

$$L' = \alpha_{Pb(Y)} * \alpha_{NR(H)} * L \qquad (1)$$

where $\alpha_{Pb(Y)}$ is a correction factor for the side reactions of the lead ions and $\alpha_{NR(H)}$ is a correction factor for the reaction between nitroresorcinate and hydrogen ions.

Based on calculations of the conditional solubility product it can be established that lead 2,4,6-trinitroresorcinate can be dissolved in the presence of 0,01 M of both NTA and EDTA. On the other hand 4-mononitroresorcinate is a very weak dibasic acid, which is difficult to dissolve at lower pH values. As a result the pH value should be above 7 (approx.) to dissolve the lead mononitroresorcinates in the presence of a complexing agent.

MULTI-COMPONENT SYSTEMS

In the analysis of a multi-component system the differential pulse technique is preferrable to other polarographic techniques, since this technique gives a greater selectivity and sensitivity. The differential pulse polarogram has the form of a derived graph of the DC polarogram and under favourable test conditions separate peaks are obtained in the reduction of different compounds and functional groups in the molecule, e.g. poly-nitro aromates.

The current at a given potential (usually the peak current i_p at the peak potential E_p) as a function of the concentration can be given by the following simplified relation:

$$i = k\,c \qquad (2)$$

where k is a constant which is dependent amongst other things on the pulse amplitude. With increasing pulse amplitude the peak current increases, but at the same time the peak width increases which means that the selectivity is reduced.

The total current at a given potential for a solution containing several reducible compounds is equal to the sum of the currents for the individual compounds; i.e. the current is additive on condition that no chemical reactions take place between the compounds or the reaction products. The following relationship can be written for the total current:

$$i = \sum_{i} k_i\, c_i \qquad (3)$$

Since the polarographic reduction of organic compounds and metal ions is affected both by the composition of the solvent and its pH value, one can often find differences in the differential pulse polarograms sufficiently large for analytical purposes by choosing suitable test conditions. It is then possible to distinguish between two extremes, namely the completely overlapping polarograms and the completely separate polarograms. In the case when the polarograms for the individual components are completely separate and the current between the polarograms follows the base line the analysis of the components can be made quite independent of one another.

REDUCTION OF NITRO GROUPS

The nitro group is commonly reduced in two stages to amine via hydroxyle amine with 4 and 2 electrons respectively:

$$RNO_2 + 4e + 4H^+ = RNHOH + H_2O \text{ and} \qquad (4)$$

$$RNHOH + 2e + 2H^+ = RNH_2 + H_2O \qquad (5)$$

at which two separate polarographic peaks are obtained under certain conditions.

The reaction mechanism for reduction of aromatic nitrocompounds is dependent not only on the number of nitro groups but also on their relative positions in the aromatic ring, on other functional groups and naturally even on the pH value of the solution and on the solvent. Under certain test conditions the reduction of the individual nitro groups of aromatic poly-nitro compounds can be distinguished and it is even possible to demonstrate the step-by-step reduction via hydroxyle amine.

Aromatic poly-nitro compounds are reduced within the potential range -0.2 V to -0.8 V. In water solutions containing methanol the reduction is displaced toward the more negative values with increasing methanol content.

REDUCTION OF LEAD IONS AND LEAD COMPLEXES

A metal ion, or rather, the hydrate complex of the metal ion in a water solution is reduced at a dropping mercury electrode according to the reaction:

$$M^{z+} + ze + Hg = M(Hg) \tag{6}$$

The half-wave potential for lead ions in a water solution with potassium chloride as electrolyte has a value of approx. - 0.4 V measured against Ag/AgCl electrode, i.e. lead ions are reduced within the same potential range as the nitro group.

In the presence of a complexing agent the half-wave potential is displaced toward more negative potentials for reduction of a metal complex according to the reaction:

$$MY_n + ze + Hg = M(Hg) + nY \tag{7}$$

where the charges have been left out for the sake of simplicity.

The displacement of the half-wave potential is described by the following equation:

$$dE = E^k_{1/2} - E_{1/2} = - \frac{RT}{zF} \ln K_{MY_n} [Y]^n \tag{8}$$

where:

$E^{k}_{1/2}$ = the half-wave potential for the metal complex

$E_{1/2}$ = the half-wave potential for the metal ion

K_{MY_n} = the stability constant for the metal complex

z = the number of electrones participating in the electrode reaction

From equation (8) it is apparent that the displacement of the half-wave potential toward more negative potentials for reduction of a metal complex increases with increasing stability of the complex. Also the half-wave potential for the metal complex is displaced toward more negative potentials when the concentration of ligand increases.

In the presence of complexing agents such as EDTA and NTA the displacement of the half-wave potential is so great that the differential pulse polarogram for the lead complex is altogether separated from the polarograms for the nitroresorcinates. With lead ions the EDTA and NTA form 1:1 complexes with the stability constants log K = 18.0 and log K = 11.8 respectively. Since the EDTA and NTA are multibasic acids the polarographic analysis of lead in the form of a complex should take place in neutral or alkaline solution. The effect of the reactions of the complexing agent with hydrogen ions can be taken into account with a side reaction coefficient $\alpha_{Y(H)}$ (3).

Since lead, either in the form of lead ions or a lead complex, is reduced with two electrons and a nitrogroup with six electrons the analysis of a nitrocompound will result in a sensitivity that is approximately 3 times greater than the analysis of lead.

EXPERIMENTAL

Apparatus

A Metrohm Polarecord E 506 was used for the polarographic analyses. The differential pulse technique was used with a pulse amplitude of 40 mV and a drop time of 3 seconds. The reference electrode was an Ag/AgCl electrode (Metrohm EA 427) and the auxiliary electrode a Pt electrode (Metrohm EA 285). The scanning rate was 2.67 mV/s. The solutions were de-aerated by passing nitrogen through the solution for about 10 minutes before recording of the polarogram. The polarograms were recorded at a temperature of 25° C.

Reagents

Electrolyte. Ammonium acetate with p a purity (E. Merck), Na_2EDTA (= disodium salt of ethylenediaminetetraacetic acid) with purity p a (E. Merck) and NTA with purity p a (E. Merck) were used. Sodium hydroxide with purity p a (E.Merck) was used for adjusting pH to the desired value.

Nitroresorcinols. Stock solutions with a concentration of approx. 3 mM were obtained by dissolving nitroresorcinols with technical purity in distilled water containing either 0.013 M Na_2EDTA and 0.05 M NH_4Ac or 0.013 M NTA, 0.05 M NH_4Ac and 0.01 M NaOH. In addition, 0.1 g of sodium hydroxide per 0.1 litre was added to the stock solutions of 2-mononitroresorcinol.

Lead acetate. A stock solution with a concentration of 3 mM was obtained by dissolving p a lead acetate, $(CH_3COO)_2Pb*3H_2O$, (E. Merck) in 0.013 M Na_2EDTA.

RESULTS

Analysis of lead

To obtain separate differential pulse polarograms for lead and nitroresorcinols lead should be transferred to a stable complex, either a Pb-EDTA complex or a Pb-NTA complex. The conditional stability constant for the Pb complex is on the acidic side affected by the reactions of the complexing agent with hydrogen ions and on the alkaline side by the lead reaction with hydroxide ions. Mixed complexes can also be generated in the presence of ammonium ions or ammonia.

To find the most suitable test condition for lead analyses differential pulse polarograms for lead have been recorded in the presence of both 0.013 M EDTA and 0.013 M NTA for various pH values. The solutions also contain 0.065 M NH_4Ac.

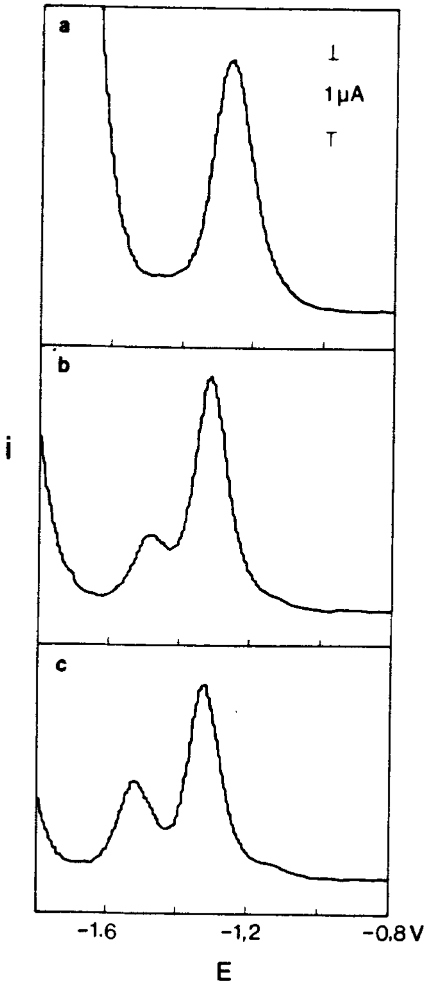


FIGURE 1

Differential pulse polarogram for 0.06 mM lead in the presence of 0.013 M EDTA and 0.065 M NH_4Ac at: a) pH = 5.95, b) pH = 7.71 and c) pH = 8.86.

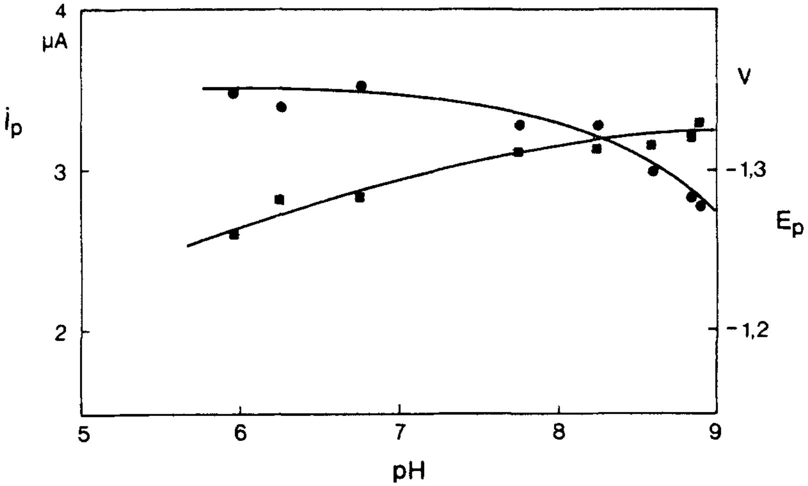


FIGURE 2

Peak current i_p (●) and peak potential E_p (■) as a function of pH in differential pulse polarographic analysis of 0.06 mM lead in the presence of 0.013 M EDTA and 0.065 M NH_4Ac.

The results of analyses of lead in the form of an EDTA complex are presented in Figures 1 and 2. With a pH value of 6 only one well defined peak is obtained at a potential of approx. -1.25 V. With an increased pH value the height of the peak is reduced and the peak potential is displaced toward more negative values whilst a new peak begins to appear at a more negative potential, which indicates that another lead complex is formed.

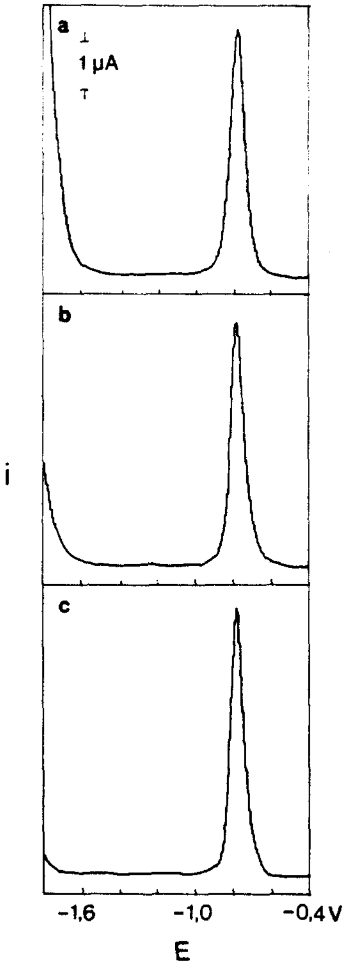


FIGURE 3

Differential pulse polarogram for 0.06 mM lead in the presence of 0.013 M NTA and 0.065 M NH_4Ac at: a) pH = 5.83, b) pH = 6.84 and c) pH = 8.86.

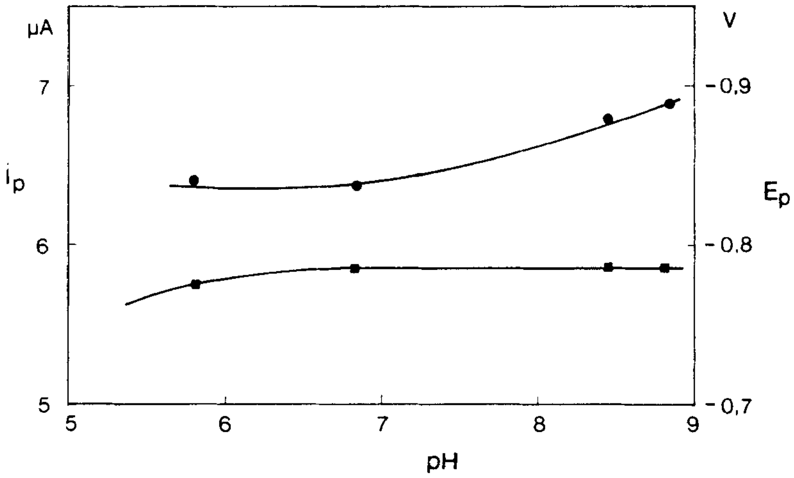


FIGURE 4

Peak current i_p (●) and peak potential E_p (■) as a function of pH in differential pulse polarographic analysis of 0.06 mM lead in the presence of 0.013 M NTA and 0.065 M NH_4Ac.

Analysis of the lead content in lead nitroresorcinates in the form of an EDTA complex by differential pulse polarography should preferably be made at a pH value of 6.

The results of analyses of lead in the form of an NTA complex are presented in Figures 3 and 4. Only one, and in fact a well defined, peak is obtained at approx. -0.8 V within the tested pH range. At pH values above approx. 6.5 the peak potential is independent of the pH of the solution. However, the peak current increases somewhat with increasing pH value. Since the Pb-NTA complex is reduced at a less negative potential than the Pb-EDTA complex an improved separation of the peak form the background current is obtained.

The analysis of the lead content in lead nitroresorcinates in the form of a Pb-NTA complex can be carried out within a greater pH range than in the form of a Pb-EDTA complex.

Analysis of nitroresorcinates

Differential pulse polarograms for 0.06 mM solutions of 2-mononitroresorcinol, 2,4-dinitroresorcinol and 2,4,6-trinitroresorcinol in the presence of 0.013 M EDTA and 0.065 M NH_4Ac at a pH value of 5.96 are shown in Figure 5. From the figure it is seen that one peak is obtained for 2-mononitroresorcinol and two for 2,4-dinitroresorcinol and 2,4,6-trinitroresorcinol. The reduction for two of the nitro groups in 2,4,6-trinitroresorcinol coincide and only two peaks are therefore obtained which have different heights.

In Table 1 the peak potentials have been listed for the three nitroresorcinols. From the table it can be seen that the difference between the peak potential for the peak of the 2-mononitroresorcinol and the first peak of the 2.4-dinitroresorcinol is approx. 0.02 V. The peak potential for the peak of the 2-mononitroresorcinol and the first peak of the 2,4,6-trinitroresorcinol are virtually at the same potential. A difference of 0.05 V is obtained between the peak potentials for the second peak of 2,4-dinitroresorcinol and 2,4,6-trinitroresorcinol.

TABLE 1

Peak potentials for 2-mononitroresorcinol, 2,4-dinitroresorcinol, 2,4,6-trinitroresorcinol.

Compound	Peak No 1	Peak No 2
2-mononitroresorcinol	- 0.340 V	
2,4-dinitroresorcinol	- 0.320 V	- 0.448 V
2,4,6-trinitroresorcinol	- 0.336 V	- 0.496 V

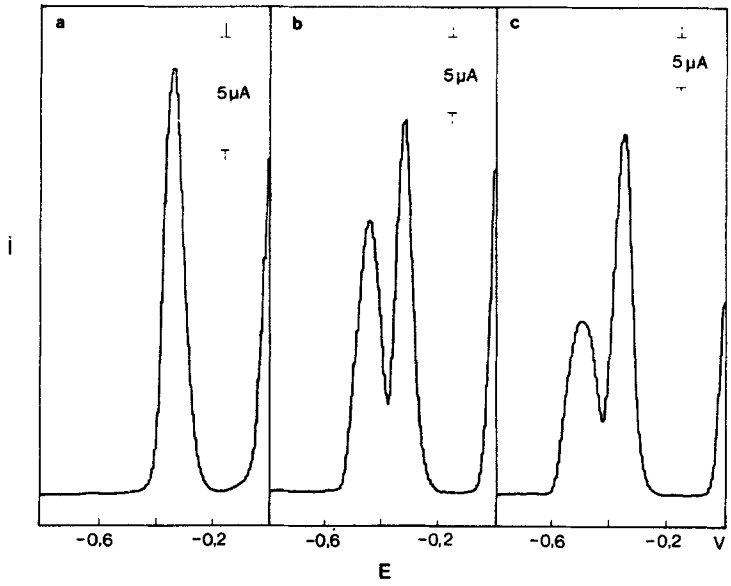


FIGURE 5

Differential pulse polarogram for 0.06 mM of a) 2-mononitroresorcinol, b) 2,4-dinitroresorcinol c) 2,4,6-trinitroresorcinol in the presence of 0.013 M EDTA and 0.065 M NH_4Ac at pH 5.96.

The sum of the peak currents for 0.06 mM solutions of 2-mononitroresorcinol, 2,4-dinitroresorcinol and 2,4,6-trinitroresorcinol has been determined to 18.60 uA, 42.25 uA and 58.00 uA respectively. The relationship between the peak currents for 2-mononitroresorcinol: 2,4-dinitroresorcinol: 2.4.6-trinitroresorcinol is 1:2.27:3.12 which agrees well with the number of nitro groups in the molecule.

Analysis of lead nitroresorcinates

Three different lead nitroresorcinates, namely lead-2-mono-nitroresorcinate, lead-2,4-dinitroresorcinate and lead-2,4,6-trinitroresorcinate-monohydrate, have been analysed. The samples were dissolved in the presence of both EDTA and NTA, and lead was analysed both in the form of an EDTA complex and an NTA complex.

A great advantage of the method is that both lead and nitroresorcinate contents can be established in one sample. The reference solutions of lead and nitroresorcinols with the same EDTA or NTA concentration and at the same pH value as the sample solutions were used to evaluate the result.

When the lead nitroresorcinates were analysed approx. 0.03 mMol, corresponding to 100 mg lead-2-mononitroresorcinate, 120 mg lead-2,4-dinitroresorcinate and 140 mg lead-2,4,6-trinitroresorcinate-monohydrate were dissolved in 100 mL of distilled water containing 2 g of Na_2EDTA and 0.4 g of NH_4Ac or 0.5 g of NTA and

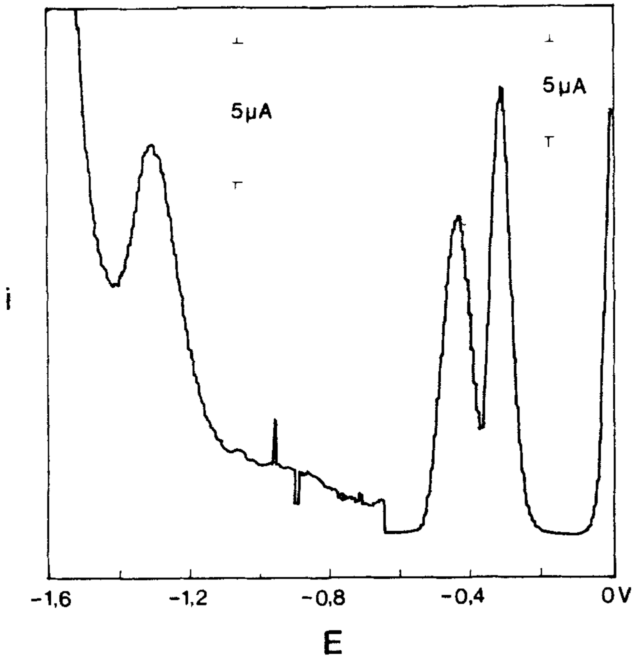


FIGURE 6

Differential pulse polarographic analysis of lead-2,4-dinitroresorcinate, 2.4 mg/100 mL in the presence of 0.013 M EDTA and 0.065 M NH_4Ac at pH 5.96.

0.1 g of NaOH. In addition 0.1 g NaOH was added to the lead-2-mononitroresorcinate solution. For the polarographic recording 1 mL of the solution was diluted to exactly 50 mL with distilled water containing 5 g of Na_2EDTA/L and 5 g of NH_4Ac/L or 0.25 g NTA/L, 1 g NaOH/L and 5 g NH_4Ac/L. The differential pulse polarograms were recorded form 0 V to -1.6 V.

In Figure 6 is shown a differential pulse polarogram for analysis of lead-2,4-dinitroresorcinate in the

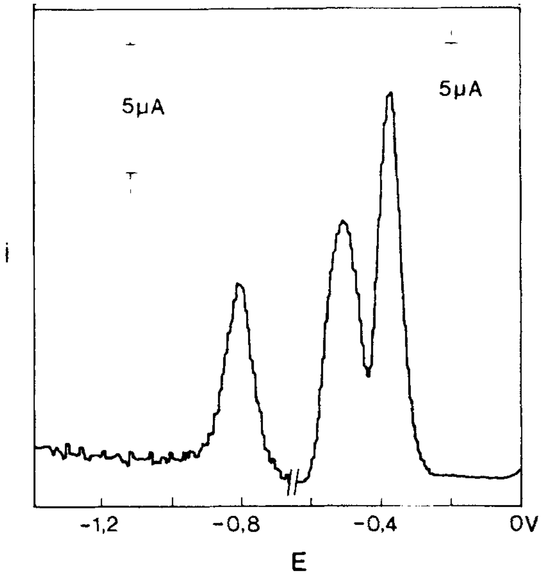
TABLE 2

The results of the analysis of three different lead nitro-rosorcinates in the presence of EDTA.

COMPOUND	Pb [%]	NITRORESORCINATE [%]	SUM [%]
Lead-2-mononitroresorcinate	57.31	38.60	95.91
	56.00	38.76	94.76
	55.30	38.33	93.63
	55.68	38.31	93.99
	57.26	38.42	94.68
	56.26	38.42	94.68
Lead-2,4-dinitroresorcinate	50.24	49.66	99.90
	48.46	48.83	97.29
	48.35	49.55	97.90
	50.50	49.29	99.79
	49.56	48.88	98.44
	49.42	49.24	98.66
Lead-2,4,6-trinitro-resorcinate-monohydrate	44.54	56.86	101.40
	44.70	56.23	100.93
	44.73	57.66	102.39
	45.78	56.74	102.52
	46.12	55.94	102.06
	45.17	56.69	101.86

presence of EDTA. A higher sensitivity has been used when recording the peak for the lead EDTA complex.

The results of the analysis of lead and nitroresorcinate contents of the various lead nitroresorcinates are summarised in Table 2. A somewhat too low content of lead-2-mononitroresorcinate was



<u>FIGURE 7</u>

Differential pulse polarographic analysis of lead-2,4-dinitroresorcinate, 2,4 mg/100 mL in the presence of 0.013 M NTA and 0.065 M NH_4Ac at pH 6.52.

obtained which indicates that the product contains an impurity or possibly hydroxide and water. For lead-2,4,6-trinitroresorcinate-monohydrate one water molecule was included in one 2.4.6-trinitroresorcinate molecule. The somewhat too high total content for this product can be explained by the fact that the product contains slightly less than one water molecule per lead-2,4,6-trinitroresorcinate molecule.

TABLE 3

The results of the analysis of three different lead nitroresorcinates in the presence of NTA.

COMPOUND	Pb [%]	NITRORESORCINATE [%]	SUM [%]
Lead-2-mononitroresorcinate	58.54	37.54	96.08
	59.60	38.85	98.45
	60.08	37.67	97.75
	59.88	38.52	98.40
	59.20	38.69	97.89
	59.46	38.25	97.71
Lead-2,4-dinitroresorcinate	51.02	48.52	99.54
	53.61	48.05	101.66
	49.52	48.23	97.75
	50.97	47.03	98.00
	52.79	47.98	100.77
	51.58	47.96	99.54
Lead-2,4,6-trinitroresorcinate-monohydrate	45.67	56.91	102.58
	47.51	56.23	103.74
	43.83	56.25	100.08
	45.30	56.00	101.30
	45.01	56.78	101.79
	45.46	56.43	101.90

In Figure 7 is shown a differential pulse polarogram for analysis of lead-2,4-dinitroresorcinate. A higher sensitivity was used, even in this case, when recording the peak for the Pb-NTA complex. From the figure it will be seen that the peak for the Pb-NTA complex and the two peaks for the 2,4,6-trinitro-

TABLE 4

The results of the analysis of a mixture of lead-2-mononitroresorcinate and lead-2,4-dinitroresorcinate in the presence of NTA.

Pb [%]	2-MONONITRORESORCINATE [%]	2,4-DINITRORESORCINATE [%]
48.15	22.64	29.01
48.10	23.93	27.97

resorcinate are completely separate and that a base line for the Pb-NTA complex is easier to find than for the peak of the Pb-EDTA complex.

The Pb-EDTA complex is more stable than the Pb-NTA complex, which means that the displacement of the half-wave potential becomes greater. A comparison of the polarograms in Figures 6 and 7 shows that an evaluation of the polarograms is easier to carry out when the lead is analysed in the form of an NTA complex.

The result of the analysis of lead and nitroresorcinate contents of the various lead nitroresorcinates has been listed in Table 3. The results agree with the results obtained in the analysis in the presence of EDTA with the difference only that a somewhat higher lead content was obtained for the lead-2-mononitroresorcinate. This can be explained by the difficulty in finding a correct baseline for the peak of the Pb-EDTA complex.

Mixtures of two different lead nitroresorcinates can also be analysed by differential pulse polarography. The example chosen is a mixture of lead-2-mononitroresorcinate and lead-2,4-dinitroresorcinate. The most reliable results are obtained by determining the lead content based on the lead peak and the 2,4-dinitroresorcinate content based on the second nitro group peak of the molecule at approx. -0.45 V. The 2-mononitroresorcinate content is then calculated as the difference. In Table 4 are shown the results of an analysis of a sample of unknown composition.

DISCUSSION

Differential pulse polarography can be used both for a qualitative and quantitative analysis of individual lead nitroresorcinates and mixtures of different nitroresorcinates in solution containing a complexing agent such as EDTA or NTA. The evaluation of the differential pulse polarograms is easier to carry out when lead is analysed in the form of an NTA complex, although the lead nitroresorcinates are somewhat more soluble in the presence of EDTA. Naturally other lead nitroresorcinates than those described, such as basic lead trinitroresorcinate, $Pb(OH)_2TNR$, can be analysed. It is also possible to analyse lead nitroresorcinates and other components such as lead azide and tetrazene polarographically. It is possible, though, that other solutions should be used for dissolving the sample. Other solutions and electrodes, too, are conceivable when recording the polarograms. For example, azide can be analysed voltammetrically at a carbon paste electrode in an acetate solution at a pH value of 4.6 (4).

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