Square-wave polarographic determination of lead(II) and zinc(II) in vinyl acetate

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In this paper the method of treatment of vinyl acetate with respect to subsequent determination of Pb(II) and Zn(II) by the method of square-wave polarography is described. The determinations were evaluated by the method of standard additions. The determined concentrations in vinyl acetate are: $\varrho(\mathrm{Pb}) = (33.6 \pm 3.6)$ ng cm^{-3} and $\varrho(\mathrm{Zn}) = (20.7 \pm 5.5)$ ng cm^{-3}.

В работе описан способ обработки винилацетата с учетом дальнейшего определения Pb(II) и Zn(II) методом квадратноволновой полярографии. Количественная оценка проводилась методом стандартных прибавок. Были найдены следующие концентрации в винилацетате: $\varrho(\mathrm{Pb}) = (33{,}6 \pm 3{,}6)$ нг см$^{-3}$ и $\varrho(\mathrm{Zn}) = (20{,}7 \pm 5{,}5)$ нг см$^{-3}$.

Besides added stabilizers, vinyl acetate also contains small amounts of heavy metals (Zn, Pb, Cu, Fe, *etc.*) the content of which must be known from the view-point of subsequent processes. We concentrated our attention on the determination of Pb and Zn. Zinc may occur in vinyl acetate because zinc acetate is frequently used as a catalyst. As for the choice of methods, we paid attention to electrochemical methods, especially square-wave polarography [1—7] which enables us in reversible systems to determine mass fractions down to 10^{-5} %.

Experimental

The polarographic measurements were performed with a square-wave polarograph OH 104 (Radelkis, Budapest) in three-electrode connection. For determining Pb and Zn, we used the following procedure: 100 cm^3 of vinyl acetate (VAC) were evaporated *in vacuo* and the residue was mineralized with 1 cm^3 of concentrated chemically pure H_2SO_4 into which 1—2 drops of concentrated anal. grade HNO_3 were added. The nearly dried sample was diluted to 25 cm^3 and 10 cm^3 of this solution was pipetted for one determination. The determination of Pb(II) was carried out directly in acid medium at the sensitivity of 8×10^{-9}

A/div and amplitude of 20 mV. Zn(II) was determined after adjusting pH to the value of 6.5—7 by addition of isothermally distilled ammonia. The sensitivity of 6×10^{-9} A/div and amplitude of the superimposed alternating voltage of 20 mV were used for determining Zn(II). The method of standard addition was applied to the determination of both cations. It was put into practice by five additions of 50 mm^3 of Pb(II) ($c(Pb(II)) = 10^{-4}$ mol dm^{-3}) or Zn(II) ($c(Zn(II)) = 2.375 \times 10^{-4}$ mol dm^{-3}). The content of the determined metals was ascertained by processing the concentration dependence by means of linear regression as the section on the axis of concentration. For comparison, we also present the results obtained with a polarograph PA 3 (Laboratorní přístroje, Prague) in differential mode, stationary dropping mercury electrode, drop time of 2 s, sensitivity 14, amplitude of 50 mV, and recording rate of 2 mV/s, the samples having been processed in the same manner.

Since chemically pure sulfuric acid contains trace amounts of Pb, Zn, and other elements, we processed blank samples under equal conditions and subtracted the obtained background.

Results and discussion

The current procedure of sample processing for determination of metals in organic material is mineralization by boiling with concentrated acids. The drawback of this method consists in bringing the determined metals in the sample with addition of the used acids. These amounts are not negligible in trace analysis and the results of analyses must be, therefore, corrected for blank test. Another drawback is tediousness of mineralization. As for analytical method, we may also use a direct polarographic determination of metals in nonaqueous medium without preceding processing of sample. This procedure involves mixing of VAC with a convenient polar solvent (dimethylformamide, dimethyl sulfoxide, *etc.*). Then the conductivity is to be adjusted by addition of an electrolyte soluble in this medium. The drawback of this procedure is tedious purification of solvents and quaternary salts as well as dilution of the sample.

This procedure is also improper for industrial control laboratories because of toxicity of the used substances and, for this reason, we abandoned it.

In the course of extractive processing, the cations pass into the aqueous phase of the used acid and simultaneously hydroquinone which is present in concentrations higher by decimal order also passes into the aqueous phase and subsequently the product of its spontaneous oxidation is polarographically reduced in the region from -0.8 V to -1.2 V where the cathodic signal of Zn(II) appears, too. As for other methods of VAC processing, we used mineralization after preceding acid hydrolysis of VAC in dilute sulfuric acid. Before mineralization, vinyl acetate must be carefully hydrolyzed because it rapidly reacts with acids. The results of square-wave polarographic determination of Zn subsequent to hydrolysis and

Table 1

Determination of Zn in a sample processed by hydrolysis and subsequent mineralization

Mineralizate	*1*	*2*	*3*	*4*	*5*	*6*
Total mass concentration of Zn in VAC and background/(μg cm^{-3})	0.89	1.29	1.43	1.24	0.99	0.99

mineralization exhibit considerable fluctuations (Table 1). The mean concentration of Zn in a sample is $\varrho = 1.14$ μg cm^{-3} while the concentration of Zn corresponding to a blank test is $\varrho = 1.0$ μg cm^{-3}. It follows from these results that the amount of Zn introduced into a sample is much greater than the amount of Zn present in VAC itself. Therefore we abandoned this procedure.

In order to obtain a certain information about the content of Zn and other metals in VAC, we removed the main component, *i.e.* VAC, by evaporation *in vacuo* and determined Zn and Pb in the residue remaining after mineralization with the

Table 2

Determination of Pb in a sample processed by evaporation and subsequent mineralization with 1 cm^3 of H_2SO_4

Mineralizate	Found mass of Pb/μg	Mass concentration of Pb in VAC after subtracting background ϱ/(μg cm^{-3})
1	1.478	0.037
2	0.804	0.020
3	1.736	0.043
3	1.322	0.033
4	1.584	0.040
4	1.368	0.034
5	1.540	0.039
5	1.201	0.030
5	0.850	0.021
6	1.160	0.029
6	1.782	0.045
6	1.244	0.031
7	1.326	0.033
7	1.408	0.035
8	1.346	0.034

$\bar{\varrho} = 0.0336$ μg cm^{-3}, $s = 6.77 \times 10^{-3}$ μg cm^{-3}, $L_{1,2} = (0.0336 \pm 0.0036)$ μg cm^{-3}.

$$s = \sqrt{\frac{\overline{\Sigma(\varrho_i - \bar{\varrho})^2}}{n-1}}; \quad L_{1,2} = \bar{\varrho} \pm s \cdot t/\sqrt{n}.$$

possibly smallest volume of acid (1 cm^3 of concentrated chemically pure H_2SO_4). Besides inorganic components, the residue also contains hydroquinone which, however, decomposes by mineralization with H_2SO_4 in the course of five minutes. After this treatment, the sample is diluted and used for the determination of Pb(II) which exhibits a cathodic peak with the maximum at -0.42 V against SCE. The half-width of this peak is approximately 50 mV, which gives evidence of a reversible two-electron reduction of Pb(II) to Pb. As the half-width of the peak was entirely constant for all concentrations of Pb(II), we evaluated only the height of this peak. The results of Pb(II) determination corrected for blank test are summarized in Table 2. The background represented 36 % of the total signal originating in Pb(II) determination provided that only 1 cm^3 of H_2SO_4 was used for mineralization of the dry residue remaining from 100 cm^3 of VAC.

Zn(II) was determined in neutral medium where the peak was higher and increased with concentration more rapidly than in the recommended medium of the ammoniacal buffer solution. In neutral medium Zn(II) is reduced at -1.03 V against SCE. The half-width of the peak is 60 mV. The results of Zn(II) determination are given in Table 3.

Table 3

Determination of Zn in a sample processed by evaporation and subsequent mineralization with 1 cm^3 of H_2SO_4

Mineralizate	Found mass of Zn/μg	Mass concentration of Zn in VAC after subtracting background $\varrho/(\mu g\ cm^{-3})$
1	0.854	0.021
2	0.482	0.012
3	0.652	0.016
4	1.040	0.026
5	1.010	0.025
6	1.118	0.028
7	0.698	0.017

$\bar{\varrho} = 0.0207\ \mu g\ cm^{-3}$, $s = 5.93 \times 10^{-3}\ \mu g\ cm^{-3}$, $L_{1,2} = (0.0207 \pm 0.005)\ \mu g\ cm^{-3}$.

$$s = \sqrt{\frac{\Sigma(\varrho_i - \bar{\varrho})^2}{n-1}}\ ; \quad L_{1,2} = \bar{\varrho} \pm s \cdot t/\sqrt{n}.$$

On the basis of many determinations using different methods of VAC processing as well as on the basis of our results given in Tables 2 to 4, we may unambiguously recommend the method involving evaporation, subsequent mineralization and

Table 4

Determination of Pb in samples of VAC processed by evaporation and subsequent mineralization with 1 cm^3 of concentrated H_2SO_4
Measured by differential impulse polarography with an instrument PA 3

Mineralizate	Found mass of Pb/μg	Mass concentration of Pb in VAC after subtracting background $\varrho/(\mu g\ cm^{-3})$
1	1.006	0.025
1	1.192	0.030
2	1.392	0.035
2	1.996	0.050

$\bar{\varrho} = 0.035\ \mu g\ cm^{-3}$, $s = 1.08 \times 10^{-2}\ \mu g\ cm^{-3}$, $L_{1,2} = (0.035 \pm 0.017)\ \mu g\ cm^{-3}$.

square-wave polarographic determination. Thus we analyzed VAC and found mass concentrations $\varrho(Pb) = (33.6 \pm 3.6)$ ng cm^{-3} and $\varrho(Zn) = (20.7 \pm 5.5)$ ng cm^{-3} in VAC.

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