# Determination of vinyl chloride and vinyl acetate in working atmosphere

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The described method of determination of the monomers of vinyl chloride and vinyl acetate in working atmosphere enables us to determine these chemical contaminants in the presence of each other by gas chromatography after retaining them on activated carbon. The elaborated sampling of air is appropriate for stationary or personal sampling of contaminants with sampling tube or passive dosimeters. The limit of determination of the method requiring a packing column containing 10 % of FFAP on Chromosorb W/AW or Chromaton N Super is 0.06 mmol dm<sup>-3</sup> (3.7  $\mu$ g cm<sup>-3</sup>) of vinyl chloride and 0.05 mmol dm<sup>-3</sup> (4.4  $\mu$ g cm<sup>-3</sup>) of vinyl acetate, which represents the concentration of 5 mg m<sup>-3</sup> of vinyl chloride or vinyl acetate provided that 3 dm<sup>3</sup> of air have been sampled. The optimum exposure of dosimeters is from 1 to 3 h. The precision and accuracy of the method was tested by model and field sampling and statistical evaluation of the sampling and determination of contaminants.

Описан метод определения мономеров винилхлорида и винилацетата в воздухе рабочих помещений, позволяющий определить эти вредные вещества при их одновременном нахождении методом газовой хроматографии после отбора на активный уголь. Разработанный способ отбора образца воздуха пригоден для стационарного и индивидуального отбора вредных веществ на отборочную трубку или пассивные дозиметры. Предел определения этим методом на колонке 10 % FFAP на Хромосорбе W/AW или Хроматоне N Супер составляет 0,06 ммоль дм<sup>-3</sup> (3,7 мкг см<sup>-3</sup>) винилхлорида и 0,05 ммоль дм<sup>-3</sup> (4,4 мкг см<sup>-3</sup>) винилацетата, что при отборе 3 дм<sup>3</sup> воз-

духа представляет концентрацию  $5\,\mathrm{mr\,m}^{-3}$  винилхлорида или винилацетата в воздухе. Оптимальная экспозиция дозиметров — от 1 до 3 часов. Точность и верность метода были проверены на модельных отборах и отборах в производственных условиях и статистической обработкой результатов отборов и определения содержания вредных веществ.

The analytical methods of determination of vinyl chloride and vinyl acetate in working atmosphere are based on determination of the double bond of the vinyl group or chlorine of vinyl chloride, oxidation of vinyl chloride or vinyl acetate and identification and determination of substances by spectrophotometry or gas chromatography.

If a toxic substance is captured from the streaming analyzed air on solid sorbent in a sampling tube, it is adsorbed on the surface of the sorbent. If the time of sampling is extended, the sorbent is gradually saturated in the course of dynamical adsorption until the full saturation is reached. From the view-point of efficiency of capture of substances on a sorbent, it is necessary to fix conventionally the required efficiency of capture of substances on a sorbent. This efficiency corresponds to 95-99 %, from which it results that the sampling should be finished in a certain limited time at which a break-through of the substance in the sorbent appears. The break-through is characterized by the time moment in which 1-5% of the input concentration of the substance is to be determined at the exit from the sorbent. The limited time of sampling break-through in the dynamical method is given for a certain type of sorbent and the substance amount may be calculated by using the Mecklenburg equation [1] or estimated according to Nelson and Harder [2]. The difficulties due to calculation of the break-through as well as the great differences in presented results advance the experimental study of the efficiency of sorbents in capturing toxic gases and vapours.

The development of a method for determining chemical contaminants in working atmosphere also necessitates solving the off-take and treatment of samples as well as the selection of the most convenient analytical method. The sampling of gases and vapours of contaminants was performed by using the standard method and applying the appropriate dosimeters described in paper [3]. The substances were concentrated and extracted by means of nitromethane which satisfied the requirements laid to a good extraction agent and was simultaneously convenient from the analytical point of view for gas chromatographic determination of vinyl chloride and vinyl acetate in the presence of other possible chemical contaminants in working atmosphere.

#### **Experimental**

## Instruments, equipments, and chemicals

Nitromethane and sec-butyl alcohol (s-B) used in our investigations were anal. grade chemicals. They were freshly redistilled before using them for preparation of the constituent and standard solutions. The pure and liquefied vinyl chloride (VC) and redistilled vinyl acetate (VAC) were products of the W. Pieck Chemical Works, Nováky (CSSR) and Duslo, Šaľa (CSSR), respectively.

The standard solutions of VC and VAC in nitromethane contained  $3.2 \,\mathrm{mmol}\,\mathrm{dm}^{-3}$  (200  $\mu\mathrm{g}\,\mathrm{cm}^{-3}$ ) of VC and  $2.3 \,\mathrm{mmol}\,\mathrm{dm}^{-3}$  (200  $\mu\mathrm{g}\,\mathrm{cm}^{-3}$ ) of VAC. They were prepared from the stock solutions which contained  $0.08 \,\mathrm{mol}\,\mathrm{dm}^{-3}$  (5  $\mathrm{mg}\,\mathrm{cm}^{-3}$ ) of VC in nitromethane and  $0.01 \,\mathrm{mol}\,\mathrm{dm}^{-3}$  (1  $\mathrm{mg}\,\mathrm{cm}^{-3}$ ) of VAC in nitromethane. The standard solution of s-B in nitromethane was of  $1.3 \,\mathrm{mmol}\,\mathrm{dm}^{-3}$  (100  $\mu\mathrm{g}\,\mathrm{dm}^{-3}$ ) concentration.

The glass withdrawing tubes and passive dosimeters [3, 4] were packed with activated carbon [5]. The individual sampling of atmosphere was made by means of personal sampling pumps SIPIN SP-15 (A. J. Sipin Co., USA).

The chromatographic analysis of model samples, standard solutions, and field samples was performed with a gas chromatograph Hewlett—Packard 5830 A (USA) equipped with a flame ionization detector in a packing column of 2 m length and 2.5 mm inside diameter. The column was packed with Chromosorb W/AW 150—180  $\mu m$  containing 10 % of FFAP or Chromaton N Super 125—150  $\mu m$  containing 10 % of FFAP (Lachema, Brno).

# Sampling of air

For determining VC and VAC in the presence of each other, we took 2—3 dm<sup>3</sup> of air through two withdrawing tubes in series by using the volume flow of 0.1—0.2 dm<sup>3</sup> min<sup>-1</sup>.

The maximum quantity of air for determining VAC was 20 dm<sup>3</sup> for volume flow of 0.2 dm<sup>3</sup> min<sup>-1</sup> or 15 dm<sup>3</sup> for volume flow of 0.5 dm<sup>3</sup> min<sup>-1</sup>.

The stationary or personal sampling with passive dosimeters was performed by exposing the dosimeters to working medium in respiring zone for 1—3 h.

# Processing of samples

The contaminants caught on activated carbon were extracted in a static manner by pouring the activated carbon into a ground test tube containing  $2 \,\mathrm{cm}^3$  of the extraction agent cooled to the temperature of the ice—NaCl mixture. The extraction was finished after 60 min at laboratory temperature under intermittent stirring. Then  $1 \,\mathrm{cm}^3$  of the internal standard was added to  $1 \,\mathrm{cm}^3$  of the extract. The samples warmed to room temperature are dosed in the amount of  $1 \,\mathrm{mm}^3$  into the gas chromatograph.

## Working conditions of gas chromatographic determination

Glass column packed with 10 % of FFAP (2-nitroterephthalate and poly(ethylene glycol)) on Chromosorb W/AW or 10 % of FFAP on Chromaton N Super.

Temperature of column: 343 K

Temperature of dosing room: 423 K

Temperature of flame ionization detector: 423 K

Rate of the volume flow of the carrier gas (nitrogen): 30 cm<sup>3</sup> min<sup>-1</sup>

Isothermal program: 8 min at 343 K

Rate of temperature increase: 30 °C min<sup>-1</sup> up to 393 K

Isothermal program: 20 min at 393 K

The record of analysis of the standard solution of vinyl chloride, vinyl acetate, and sec-butyl alcohol in nitromethane is represented in Fig. 1. The record of analysis of a sample of air after sampling by means of activated carbon, extraction with nitromethane,

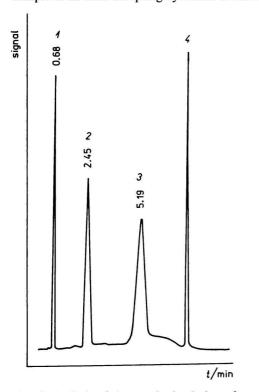


Fig. 1. Analysis of the standard solution of vinyl chloride (1) and vinyl acetate (2) with internal standard (sec-butyl alcohol) (3) in nitromethane (4); column packing: Chromaton N Super with 10 % of FFAP.

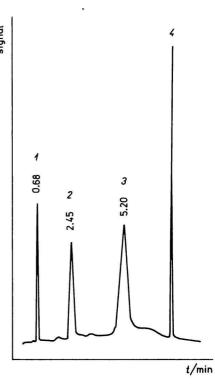


Fig. 2. Record of analysis of a sample of air drawn on activated carbon: vinyl chloride (1), vinyl acetate (2), sec-butyl alcohol (3), nitromethane (4); column packing: Chromaton N Super with 10 % of FFAP.

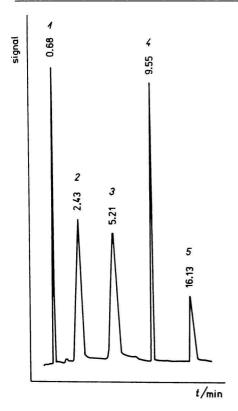
and addition of the internal standard is represented in Fig. 2. The relative elution times of contaminants are given in Table 1.

From the stand-point of qualitative analysis, we investigated the interference of acetic acid. We have found that the presence of this substance does not interfere with the determination of VC and VAC under the used conditions (Fig. 3).

Table 1

Relative elution times of substances
Elution time of sec-butyl alcohol functioning as internal standard 312 s

| F1'             |                   | Relative elution time             |                                       |  |  |  |  |  |
|-----------------|-------------------|-----------------------------------|---------------------------------------|--|--|--|--|--|
| Elution<br>wave | Substance         | Chromosorb W/AW with 10 % of FFAP | Chromaton N Super<br>with 10% of FFAP |  |  |  |  |  |
| 1               | Vinyl chloride    | 0.118                             | 0.131                                 |  |  |  |  |  |
| 2               | Vinyl acetate     | 0.457                             | 0.472                                 |  |  |  |  |  |
| 3               | sec-Butyl alcohol | Ī                                 | 1                                     |  |  |  |  |  |



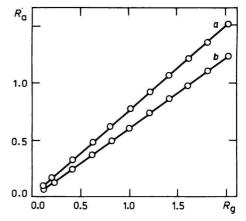


Fig. 4. Analytical calibration curve for vinyl acetate (a) and vinyl chloride (b); column packing Chromaton N Super with 10% of FFAP.

Fig. 3. Analysis of a mixture containing vinyl chloride (1), vinyl acetate (2), sec-butyl alcohol (3), nitromethane (4), and acetic acid (5); column packing: Chromaton N Super with 10 % of FFAP.

#### Analytical calibration curve

A set of ten calibration solutions was prepared. These solutions contained nitromethane as solvent, vinyl chloride and vinyl acetate in concentrations ranging from 0.06 to  $1.6\,\mathrm{mmol\,dm^{-3}}$  (5— $100\,\mu\mathrm{g\,cm^{-3}}$ ), and  $0.67\,\mathrm{mmol\,dm^{-3}}$  (50  $\mu\mathrm{g\,cm^{-3}}$ ) of sec-butyl alcohol functioning as internal standard.

The calibration solutions were dosed in the amount of 1 mm<sup>3</sup> into the gas chromatograph. The analytical calibration curve of vinyl chloride and vinyl acetate (Fig. 4) was constructed from the ratios of the planes of vinyl chloride or vinyl acetate to the plane of internal standard (sec-butyl alcohol) ( $R_a$ ) and the corresponding ratios of the concentrations of vinyl chloride or vinyl acetate to the concentration of internal standard ( $R_g$ ). The analytical calibration curves were statistically evaluated according to [6]. The characteristics of analytical calibration curves on 5% level of significance are given in Table 2. The values of the limit of determination calculated from analytical calibration curves were in good agreement with the experimental values of the limit of determination. The statistical characteristics of the *t*-test for model concentrations of substances ( $\mu$ ) which are consistent with the calculated limits of determination are given in Table 3.

The mean values  $(\bar{x})$ , standard deviations (s), interval of reliability  $(L_{\bar{x}})$ , and relative standard deviation of determination  $(s_r)$  were calculated from six independent analyses.

The reproducibility and reliability of the method is presented for six independent analyses of model samples ( $\mu_1 - \mu_3$  VC and  $\mu_4 - \mu_6$  VAC) in Table 4.

## Calculation of concentration of contaminants in atmosphere

The average mass concentration  $\varrho$  of vinyl chloride or vinyl acetate in air (mg m<sup>-3</sup>) for sampling with withdrawing tubes was calculated from the equation

$$\varrho = \frac{R_{\rm a}c_{\rm s-B}k}{KV}$$

where the symbols  $R_a$ ,  $c_{s-B}$ , K, V, and k stand for the ratio of the plane of chromatographic wave of vinyl chloride or vinyl acetate to the plane of internal standard s-B, concentration of internal standard in extraction agent (mg cm<sup>-3</sup>), analytical constant for VC and VAC (Table 2), withdrawn volume of air (m<sup>3</sup>), and coefficient of dilution (k = 4).

The average mass concentration  $\varrho_t$  of contaminant in analyzed air after sampling with passive dosimeters for time  $t \pmod{m \text{ m}^{-3}}$  can be calculated from the formula

$$\{\varrho_t\}_{\mathsf{mg}\,\mathsf{m}^{-3}} = 10^3 \cdot \frac{m_t}{DK_{\mathrm{D}}t}$$

where  $m_t$ , t, D, and  $K_D$  are mass of contaminant caught on sorbent in time interval t (µg), exposure of dosimeter (s), diffusion coefficient of substance (cm<sup>2</sup> s<sup>-1</sup>), and constant of dosimeter (cm), respectively.

Table 2 Statistical evaluation of analytical calibration curves

| Characteristics  | Vinyl chloride (VC)  | Vinyl acetate (VAC)  |
|--|--|--|
| Regression equation  | y = Kx   | y = Kx   |
| Analytical constant (K)  | 0.601  | 0.744  |
| Reliability interval of analytical constant $(L_K)$  | $0.601 \pm 0.023$  | $0.744 \pm 0.033$  |
| Reliability interval $(L_{Ky})$ of measured values $\{y\}$ as a function of values $\{x\}$ | $\{y\} = 0.601 \{x\} \pm (0.6 \times 10^{-3} + 0.5 \times 10^{-3} \{x\}^2 - 1 \times 10^{-3} \{x\})^{1/2}$ | $\{y\} = 0.744 \{x\} \pm (1.4 \times 10^{-3} + 1.1 \times 10^{-3} \{x\}^2 - 2.2 \times 10^{-3} \{x\})^{1/2}$ |
| Standard deviation $\{s_{xy}K\}$ of scatter of calibration relation                        | 0.015  | 0.022  |
| Lower limit of determination $\{K_{lim}\}$   | $0.059 \text{ mmol}$ $3.7  \mu\text{g cm}^{-3}$  | 0.051  mmol<br>$4.4 \mu\text{g cm}^{-3}$   |

Table 3

Limit of determination

| Substance | $\frac{\mu}{\mu g  cm^{-3}}$ | $\frac{\bar{x}}{\mu g  cm^{-3}}$ | $\frac{s}{\mu g  cm^{-3}}$ | $\frac{L_{\bar{x}}}{\mu g  \text{cm}^{-3}}$ | $\frac{s_r}{\%}$ | t      |
|-----------|------------------------------|----------------------------------|----------------------------|---|------------------|--------|
| VC        | 5.5                          | 5.64                             | 0.236                      | 5.64 ± 0.25                                 | 4.2              | 1.4531 |
| VAC       | 5.0                          | 4.88                             | 0.220                      | $4.88 \pm 0.23$                             | 4.5              | 1.3361 |

Table 4

Precision and accuracy of analysis of model samples

| n | $\frac{\mu}{\mu g  cm^{-3}}$ | $\frac{\bar{x}}{\mu g  \text{cm}^{-3}}$ | $\frac{s}{\mu g  \text{cm}^{-3}}$ | $\frac{L_{\bar{x}}}{\mu \mathrm{g  cm}^{-3}}$ | $\frac{s_r}{\frac{9}{6}}$ | t      |
|---|------------------------------|---|-----------------------------------|---|---------------------------|--------|
| 1 | 35.5                         | 35.03                                   | 0.946                             | 35.03 ± 0.99                                  | 2.7                       | 1.2169 |
| 2 | 52.5                         | 53.30                                   | 1.542                             | $53.30 \pm 1.62$                              | 2.9                       | 1.2669 |
| 3 | 104.5                        | 105.18                                  | 1.988                             | $105.18 \pm 2.09$                             | 1.9                       | 0.8319 |
| 4 | 30.0                         | 30.70                                   | 0.858                             | $30.70 \pm 0.90$                              | 2.8                       | 1.9984 |
| 5 | 75.5                         | 74.81                                   | 1.640                             | $74.81 \pm 1.72$                              | 2.2                       | 1.0455 |
| 6 | 98.9                         | 100.02                                  | 2.695                             | $100.02 \pm 2.83$                             | 2.7                       | 1.0907 |

Table 5

Diffusion parameters of dosimeters

|           | Diffusion parameter | of dosimeters $(D K_D)$ |                               |  |
|-----------|---------------------|-------------------------|-------------------------------|--|
| Substance | cm <sup>3</sup>     | Diffusion coefficient   |                               |  |
| _         | Dosimeter K         | Dosimeter P             | $D/\text{cm}^2 \text{s}^{-1}$ |  |
| VC        | 0.289 ± 0.026       | $0.777 \pm 0.038$       | 0.0996                        |  |
| VAC       | $0.030 \pm 0.012$   | $0.619 \pm 0.018$       | 0.0793                        |  |

The values of the product of diffusion coefficient of substance and constant of dosimeter  $(D K_D = D_k)$  given in Table 5 were experimentally determined from the amount of captured substance  $m_t$  and exposure of dosimeter t at average mass concentration of substance  $\varrho_t$  in exposure chamber [3]. These experimental values  $D_k$  and  $K_D$  were used for calculating the diffusion coefficients of vinyl chloride and vinyl acetate at the temperature of 295 K and the pressure of  $101.5 \, \text{kPa}$ .

Table 6

Equilibrium sorption power of substances on activated carbon GA-I (0.8—1.25 mm), rate of volume flow of dry air 0.5 dm³ min<sup>-1</sup>, temperature 293—295 K, pressure 101.54 kPa

| G 1 .     | Mass concentration of substance in air | Equilibrium sorption power of substance |
|-----------|--|---|
| Substance | mg m <sup>-3</sup>                     | $mgg^{-1}$                              |
| VC        | 100                                    | 9.8                                     |
|           | 300                                    | 13.2                                    |
| VAC       | 200                                    | 76                                      |
|           | 800                                    | 128                                     |

#### Results and discussion

The adsorptive ability of activated carbon was experimentally studied by using gravimetry (Table 6). The specific surface and overall porosity of the used activated carbon was  $920\,\mathrm{m^2\,g^{-1}}$  and  $1.23\,\mathrm{cm^3\,g^{-1}}$ , respectively. The break-through in the layer of sorbent in withdrawing tube was investigated by following the amount of substances in other withdrawing tube under the experimental conditions stated in Table 7. The experimental results reveal the fact that higher vapour pressures of substances and higher volume flow of air facilitate the break-through in the layer of sorbent. The personal sampling with passive dosimeters gives more reliable picture of the exposure of workers to chemical injurers. The merit of using passive dosimeters also consists in the fact that they are usable in explosive medium and their price is moderate. Owing to the values of parameter D(A/I) of dosimeters  $\bar{K}$  and  $\bar{P}$  (Table 5) which dimensionally represent the volume flow (cm<sup>3</sup> s<sup>-1</sup>) and may be compared with the volume flow during sampling of contaminants on activated carbon in withdrawing tubes, it is evident that the time of sampling must be different.

The desorption of the substances captured on activated carbon is most frequently achieved by the use of carbon disulfide. If vinyl chloride and vinyl acetate are determined in the presence of each other by gas chromatography, carbon disulfide interferes with the elution wave of vinyl acetate. However, if we used nitromethane as eluting agent, we achieved good separation of all determined components and the desorption efficiency studied by comparing the results obtained by four methods [7, 8] was 94.7—104.1 %.

The results of static desorption of the substances are presented in Table 8. A change in the ratio of mass of extraction agent and sorbent did not produce a statistically significant change in desorption efficiency.

Table 7

Break-through in 300 mg layer of activated carbon in withdrawing tube by vinyl chloride and vinyl acetate: temperature 293—298 K, pressure 100.9--102.34 kPa, relative humidity 35—52 %

| Substance | Mass concentration in air | Rate of volume flow   |              | e captured on<br>ndrawing tube)/% | Break-through in carbon layer in the first withdrawing tube |            |                          |  |
|-----------|---------------------------|-----------------------|--------------|-----------------------------------|---|------------|--------------------------|--|
|           | mg m <sup>-3</sup>        | dm³ min <sup>-1</sup> | in the first | in the second                     | after substance<br>adsorption<br>m/mg                       | after time | after air sampling V/dm³ |  |
| VC        | 500                       | 0.1                   | 97.5         | 2.5                               | 0.98  | 19         | 1.9                      |  |
|           |                           | 0.2                   | 97.8         | 2.2                               | 0.93  | 8.5        | 1.7                      |  |
|           | 250                       | 0.1                   | 97.1         | 2.9                               | 0.64  | 26         | 2.6                      |  |
|           |                           | 0.2                   | 96.6         | 3.4                               | 0.51  | 10         | 2                        |  |
|           | 50                        | 0.1                   | 95.1         | 4.9                               | 0.19  | 38         | 3.8                      |  |
|           |                           | 0.2                   | 96.1         | 3.9                               | 0.16  | 16         | 3.2                      |  |
| VAC       | 250                       | 0.2                   | 99.5         | 0.5                               | 6.9   | 138        | 28                       |  |
|           |                           | 0.5                   | 98.9         | 1.1                               | 6.5   | 52         | 26                       |  |
|           | 108                       | 0.2                   | 90.5         | 0.5                               | 3.2   | 150        | 30                       |  |
|           |                           | 0.5                   | 98.5         | 1.5                               | 2.9   | 54         | 27                       |  |
|           | 55                        | 0.2                   | 98.8         | 1.2                               | 1.3   | 118        | 24                       |  |
|           |                           | 0.5                   | 97.9         | 2.1                               | 0.9   | 34         | 17                       |  |

Table 8

Desorption efficiency of substances (DE) and standard deviations (s)

A — dynamic method, B — direct sampling of substance on carbon, C — sampling of substance in eluting solvent, D — method of phase equilibrium

|                | Sorbed amount of substance on 300 mg |      |     |      |      | Desor    | ption | efficienc | y DE/         | % and    | standa | rd devia | tion s     | :/%     |     |       |            |
|----------------|--------------------------------------|------|-----|------|------|----------|-------|-----------|---------------|----------|--------|----------|------------|---------|-----|-------|------------|
| Sub-<br>stance | of carbon                            | 7/   |     | in   | carb | on disu  | lfide |           |               |          |        | *        | in nitr    | omethai | ne  |       |            |
|                | mg                                   | A    |     | В    | 1    | (        | ]     | Г         | )             | Α        |        | В        |            | С       |     | I     |            |
|                |                                      | {DE} | {s} | {DE} | {s}  | $\{DE\}$ | {s}   | $\{DE\}$  | <b>[</b> {s}] | $\{DE\}$ | {s}    | {DE}     | <i>{s}</i> | {DE}    | {z} | {DE}  | <i>{s}</i> |
| VC             | 0.15                                 | 88.7 | 2.4 | _    | _    | 89.1     | 1.6   | 98.5      | 4.1           | 98.5     | 1.7    |          |            | 98.3    | 2.1 | 104.1 | 1.9        |
|                | 0.6                                  | 98.1 | 3.1 | _    |      | 92.5     | 3.8   | 97.6      | 3.2           | 100.4    | 3.1    | _        | _          | 99.7    | 4.1 | 101.8 | 7.1        |
| VAC            | 0.15                                 | 84.5 | 2.1 | 79.9 | 2.4  | 88.6     | 2.4   | 86.9      | 1.8           | 96.8     | 2.7    | 94.7     | 2.2        | 97.1    | 3.6 | 99.7  | 1.1        |
|                | 2.0                                  | 78.5 | 1.9 | 92.7 | 2.7  | 92.7     | 2.7   | 94.1      | 3.2           | 95.1     | 1.6    | 95.2     | 3.1        | 97.6    | 2.1 | 101.3 | 1.7        |
| VC<br>and      | 0.6                                  | 87.7 | 1.5 | _    | _    | 90.8     | 3.4   | 97.1      | 1.8           | 98.8     | 1.2    | -        | *.         | 98.1    | 1.4 | 98.5  | 2.1        |
| VAC            | 2.0                                  |      | _   | _    | _    | _        | _     | _         | _             | 97.1     | 2.1    |          | _          | 99.1    | 2.5 | 100.5 | 2.3        |

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Table 9

Statistical evaluation of model experiments with VC and VAC after sampling with dosimeters and withdrawing tube by the method of linear regression

|   | 3, 8,93                               |  | Vinyl c                                | hloride                               |  |  |                                       |                                       | Vinyl                                 | acetate                               | . 12                                  |                               |  |
|---|---------------------------------------|--|--|---------------------------------------|--|--|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|-------------------------------|--|
| Characteristics   | Dosimeter K                           |  |  | Dosimeter P                           |  |  | Dosimeter K                           |                                       |                                       | D                                     | Dosimeter P                           |                               |  |
| Number of measurements  | -                                     | 12                                     |  |                                       | 12                                     |  | 12                                    |                                       |                                       | 12                                    |                                       |                               |  |
| Regression equation $y = a + bx$ $x - \text{withdrawing tube}$ $y - \text{dosimeter}$                                   | y = 1                                 | y = 1.002x + 0.967                     |  |                                       | y = 1.017x - 0.023                     |  |                                       | y = 1.038x - 2.176                    |                                       |                                       | y = 1.035x - 1.545                    |                               |  |
| Correlation coefficient (r)   | 0.994                                 |  |  |                                       | 0.993                                  |  |                                       | 0.998                                 |                                       | 0.998                                 |                                       |                               |  |
| Standard deviation of   | 2.777                                 |  | 2.969                                  |                                       | 1.178                                  |  |                                       | 1.577                                 |                                       |                                       |                                       |                               |  |
| slope of straight line $(s_b)$<br>Standard deviation of<br>intercept on y axis $(s_a)$                                  | 0.034                                 |  | 0.037                                  |                                       | 0.014                                  |  | 0.019                                 |                                       |                                       |                                       |                                       |                               |  |
| Interval of reliability for intercept on x axis   |                                       |  |  |                                       |  |  |                                       |                                       |                                       |                                       |                                       |                               |  |
| $L(b)_1$ $L(b)_2$ for intercept on y axis   |                                       | $L(b)_1 = 0.926$<br>$L(b)_2 = 1.078$   |  |                                       | $L(b)_1 = -0.935  L(b)_2 = 1.098$      |  |                                       | $L(b)_1 = 1.007  L(b)_2 = 1.069$      |                                       |                                       | $L(b)_1 = 0.994  L(b)_2 = 1.076$      |                               |  |
| $L(a)_1$ $L(a)_2$   | $L(a)_1 = 5.219$<br>$L(a)_2 = 7.154$  |  |  | $a)_1 = -6.$<br>$a)_2 = 6.$           |  | $L(a)_1 = -4.799$<br>$L(a)_2 = 0.448$  |                                       |                                       | $L(a)_1 = -5.058$<br>$L(a)_2 = 1.969$ |                                       |                                       |                               |  |
| Zone of reliability of y<br>for x<br>$(x = 90 \text{ mg m}^{-3},$<br>$30 \text{ mg m}^{-3},$<br>$10 \text{ mg m}^{-3})$ | y <sub>1</sub><br>87.3<br>27.6<br>7.5 | y <sub>2</sub><br>91.1<br>30.6<br>10.9 | y <sub>3</sub><br>95.0<br>33.5<br>12.8 | y <sub>1</sub><br>87.4<br>26.7<br>7.7 | y <sub>2</sub><br>91.5<br>30.5<br>10.1 | y <sub>3</sub><br>95.6<br>32.3<br>13.9 | y <sub>1</sub><br>89.3<br>26.9<br>6.8 | y <sub>2</sub><br>91.3<br>28.9<br>8.2 | y <sub>3</sub> 93.2 30.9 10.6         | y <sub>1</sub><br>89.0<br>27.8<br>7.9 | y <sub>2</sub><br>91.6<br>29.5<br>9.2 | y <sub>3</sub> 94.2 32.2 12.1 |  |

Table 10

Results of field measurements in production of VC and VAC and their copolymers; simultaneous sampling with passive dosimeters and withdrawing tubes, 1, 2 — exposure in hours

| Sample |                    | Mas               | s concentration   | of substance/(mg    | m <sup>-3</sup> )   |                    | with dosimet<br>to sam | or of sampling<br>ers with respect<br>pling with<br>wing tubes |
|--------|--------------------|-------------------|-------------------|---------------------|---------------------|--------------------|------------------------|--|
|        |                    | Vinyl chlorid     | e                 |                     | Vinyl acetate       |                    |                        | %  |
|        | ĸ                  | P                 | Т                 | ĸ                   | P                   | T                  | VC                     | VAC  |
| 1      | 6.201              | 6.73 <sup>1</sup> | 5.95 <sup>1</sup> | 14.261              | 14.551              | 11.28              | 8.66                   | 21.7   |
| 2      |                    |                   |                   | 12.801              | 13.15 <sup>1</sup>  |                    |                        |  |
| 3      | 28.12 <sup>2</sup> | $29.5^{2}$        | $27.9^{2}$        | 54.61 <sup>2</sup>  | 46.92 <sup>2</sup>  | $49.40^{2}$        | 3.26                   | 2.76   |
| 4      |                    |                   |                   | 128.60 <sup>1</sup> | 137.80 <sup>1</sup> | 95.40 <sup>1</sup> |                        | 39.62  |
| 5      |                    |                   |                   |                     | $387.97^2$          | $416.03^{2}$       |                        | 12.82  |
| 6      | 6.291              | 6.521             | $6.08^{1}$        | 14.261              | 13.36 <sup>1</sup>  | 12.24 <sup>1</sup> | 5.35                   | 29.52  |
| 7      |                    |                   |                   |                     | $3.29^{2}$          | $2.54^{2}$         |                        | 4.3  |
| 8      |                    |                   |                   | $4.06^{2}$          | $4.18^{2}$          | $3.95^{2}$         |                        | 4.79   |
| 9      |                    |                   |                   | $11.52^2$           | $11.9^{2}$          | $12.3^{2}$         |                        | 8.82   |
| 10     | 39.71              | 33.9 <sup>1</sup> | 44.81             | 76.7 <sup>1</sup>   | 65.02 <sup>1</sup>  | 77.71 <sup>1</sup> | 17.86                  |  |
| 11     |                    | $3.16^{2}$        | $3.88^{2}$        |                     |                     |                    | 18.54                  |  |
| 12     | 19.11              | 20.51             | 21.71             |                     |                     |                    | 8.76                   |  |
| 13     | 88.4 <sup>2</sup>  | $79.5^{2}$        | 87.1 <sup>2</sup> |                     |                     |                    | 3.62                   |  |
| 14     | 28.8 <sup>2</sup>  | 32.7 <sup>2</sup> | 33.1 <sup>2</sup> |                     |                     |                    | 7.10                   |  |

The gas chromatographic analysis of VC and VAC in carbon disulfide was carried out with different column packings. A good separation of the standard mixtures of substances was accomplished in packing columns with Chromosorb W/AW and 10% of FFAP or Chromaton N Super and 10% of FFAP. The resolution power of these columns under the recommended conditions is R = 3.8 for vinyl chloride as well as for vinyl acetate.

The statistical evaluation of model experiments according to [6, 9] is given in Tables 9 and 10. The relative errors of determination for sampling with passive dosimeters when compared with the results obtained by the standard method of sampling in field indicate a very good agreement.

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