Determination of methyl methacrylate, butyl acrylate, and n-butyl alcohol in working atmosphere

[a]V. KOLLÁR, [b]R. KEMKA, and [c]J. TÖLGYESSY

[a]Department of Technology of Merchandise, Faculty of Commerce,
High School of Economics, CS-832 20 Bratislava

[b]Research Institute of Preventive Medicine,
CS-833 01 Bratislava

[c]Department of Chemistry and Technology of Environment,
Slovak Technical University, CS-812 37 Bratislava

A gas chromatographic method of determination of methyl methacrylate, butyl acrylate, and n-butyl alcohol in working atmosphere was developed. The aim has been to make possible simultaneous sampling of the substances from atmosphere with withdrawing tubes and passive dosimeters which are appropriate for using in all cases where the character of technology of production and processing of these substances as well as explosive atmosphere do not allow the use of classical sampling device. The limit of determination of the substances under the recommended conditions is $0.8 \ mg \ m^{-3}$. The statistical processing of model and field sampling on 5 % level of significance gave reliable results.

Разработан газово-хроматографический метод определения метилметакрилата, бутилакрилата и н-бутилового спирта в воздухе рабочих помещений. Целью было произвести одновременный отбор образцов из воздуха на отборочные трубки и пассивные дозиметры, пригодные для применения везде, где характер технологии производства и переработки данных веществ, а также взрывоопасность не позволяет применять классические отборочные приспособления. Предел определения веществ в воздухе в рекомендуемых условиях равен $0{,}8 \ мг \ м^{-3}$. Статистическая обработка модельных отборов и отборов в производственных условиях на 5 % уровне значимости дала надежные результаты.

The colorimetric and photometric methods of determination of acrylates presented in literature [1—4] are not selective and the limit of determination of total amount of acrylates does not meet the need to determine the highest admissible concentrations (HAC) which are proposed for these substances.

Podkovyrina et al. [5] were concerned with gas chromatographic analysis of some prepared mixtures of acrylates. The determination of acrylates in atmosphere by using sampling with activated carbon in withdrawing tubes is described in [6—8].

The aim of this study has been to complete the solution of the problem of determination of methyl methacrylate and butyl acrylate by taking into account the presence of n-butyl alcohol which most frequently is present in working atmosphere and to apply the method of passive dosimetry to sampling. This method either was not used in the above-mentioned investigations or its application [6] did not give reliable results when compared with the standard method of sampling by means of withdrawing tubes.

Experimental

Chemicals, solutions, instruments, and equipments

Carbon disulfide which was anal. grade reagent (Analar, England) was purified according to [9]. Isopropyl alcohol (i-P) and isobutyl alcohol (i-B) were also anal. grade chemicals (Lachema, Brno). Methyl methacrylate (MMC) and butyl acrylate (BAC) (Chemical Works, Žilina) were freshly distilled. Anal. grade n-butyl alcohol (n-B) was product of Merck A. G. (Darmstadt, GFR). Carbon disulfide with 5 volume % of isopropyl alcohol was used as extractive agent.

The concentrations of individual components in the standard solution of MMC, n-B, and BAC were $1.99 \, \text{mmol dm}^{-3}$, $2.69 \, \text{mmol dm}^{-3}$, and $1.56 \, \text{mmol dm}^{-3}$ ($200 \, \mu\text{g cm}^{-3}$), respectively. The concentration of the standard solution of i-B in extractive agent was $0.135 \, \text{mmol dm}^{-3}$ ($100 \, \mu\text{g cm}^{-3}$). The sampling was made with passive dosimeters [10] and withdrawing glass tubes [6] packed with activated carbon GA-I [9].

The gas chromatographic measurements were performed with an instrument Hewlett —Packard 5830 A (USA) equipped with a flame ionization detector. The length and inside diameter of packing glass columns were 2 m and 2.5 mm, respectively. Moreover, an infrared analyzer of gases and vapours MIRAN IA (Foxoboro, USA), pump TUR-9 Tesla (Elstroj, Prague), personal sampling pump SIPIN SP-15 (A. J. Sipin Co., USA) and wet gasometer PL-0.1 (UČP, Skuteč) were used for measurements.

Sampling of air

In short-termed sampling we take $2—5 \, \text{dm}^3$ of air while in long-termed sampling we take $20—30 \, \text{dm}^3$ of air by sucking it through two withdrawing tubes in series, the volume flow being from 0.2 to $0.5 \, \text{dm}^3 \, \text{min}^{-1}$. Provided the content of contaminants in the second withdrawing tube exceeds 5 mass % of the total amount captured in both tubes, the sample is discarded.

The stationary or personal sampling with passive dosimeters is performed by placing them in the respiring zone of workers, their exposure being 1—4 h.

Processing of samples

The contaminants concentrated on activated carbon were extracted by the static method [6, 10]. The extraction was finished in the course of 50 min under intermittent stirring at room temperature. Then 1 cm³ of the internal standard was added into 1 cm³ of the solution. The standard solution stocked at 273 K was stable and did not exhibit any concentration change in the course of 10 days.

Working conditions of gas chromatographic determination

Packing glass column of 2 m length and 2.5 mm inside diameter packed with 10 % of FFAP (2-nitroterephthalate poly(ethylene glycol)) on Chromosorb W/AW 150—180 μm or 10 % of FFAP on Chromaton N Super 125—150 μm (Lachema, Brno). Temperature of column: 343 K. Temperature of dosing room: 423 K. Temperature of detector: 473 K. Volume flow of carrier gas (nitrogen): 30 cm³ min⁻¹.
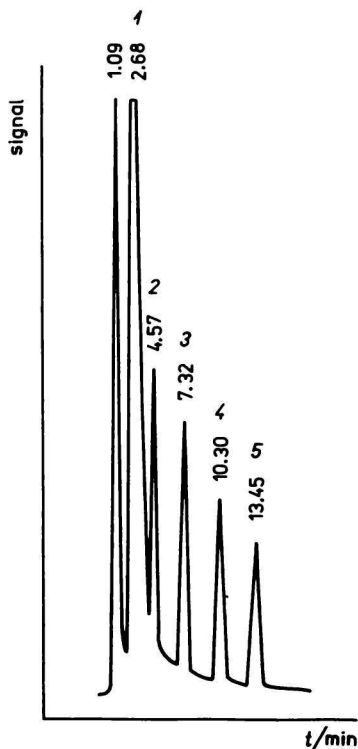

Fig. 1. Chromatogram of the standard solution of a mixture on Chromaton N Super with 10 % of FFAP.
1. Extractive agent; 2. MMC; 3. i-B; 4. n-B; 5. BAC.

The chromatographic record of the standard solution containing methyl methacrylate, n-butyl alcohol, butyl acrylate, and isobutyl alcohol in the extractive agent is represented in Fig. 1. The records of the samples of air for field measurements are in Figs. 2 and 3. The relative elution times of the substances are given in Table 1.
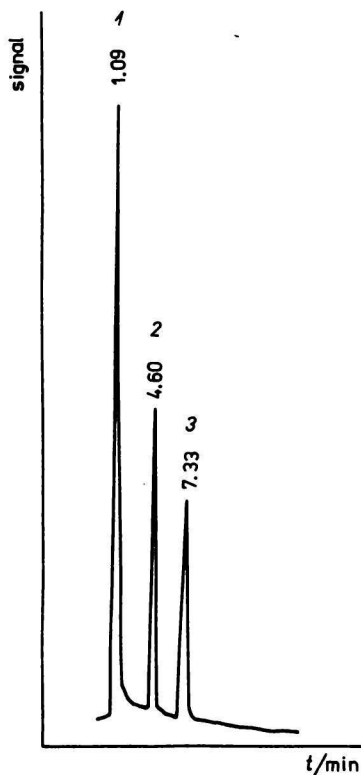

Fig. 2. Chromatogram of a field sample of atmosphere on Chromaton N Super.
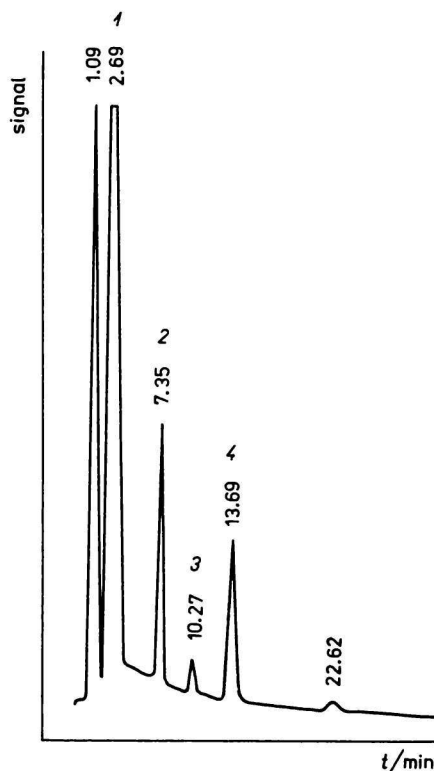*1.* Extractive agent; *2.* MMC; *3.* i-B.

Fig. 3. Chromatogram of a field sample of atmosphere on Chromaton N Super.
1. Extractive agent; *2.* i-B; *3.* n-B; *4.* BAC.

Analytical calibration curve

A set of standard solutions of the mixture of MMC, n-B, and BAC in the elution solution containing $0.67 \, \text{mmol dm}^{-3}$ ($50 \, \mu\text{g cm}^{-3}$) of the internal standard was prepared in the concentration range $0.04 \, \text{mmol dm}^{-3}$—$1.35 \, \text{mmol dm}^{-3}$ (5—$100 \, \mu\text{g cm}^{-3}$). The calibration solutions were dosed in the amount of $1 \, \text{mm}^3$ into the gas chromatograph. The analytical calibration curves of MMC, n-B, and BAC (Figs. 4 and 5) were constructed from the ratio of the areas of chromatographic waves of individual substances to the area of chromatographic wave of the internal standard (R_a) in relation to the ratio of the

164

Table 1

Relative elution times of substances
Elution time of isobutyl alcohol (internal standard) 435 s

Elution wave	Substance	Relative elution time	
		Chromosorb W/AW with 10 % of FFAP	Chromaton N Super with 10 % of FFAP
1	MMC	0.57	0.63
2	i-B	1	1
3	n-B	1.40	1.43
4	BAC	1.72	1.86

concentrations of individual substances to the concentration of the internal standard (R_g). The statistical evaluation of the analytical calibration curves according to [11] is presented in Table 2. The least concentration of the determined component in a sample that can be reliably determined by this method of analysis of working atmosphere is defined as the limit of determination. The experimental verification of the limit of determination was performed by using the analysis of model samples. The results of six independent analyses of ready-made samples containing the determined component (μ) have been statistically processed and are given in Table 3. The precision and accuracy of the method is presented by a set of the results obtained from a series of six analyses of the model samples after eliminating some distant results by means of the *t*-test (Table 4).
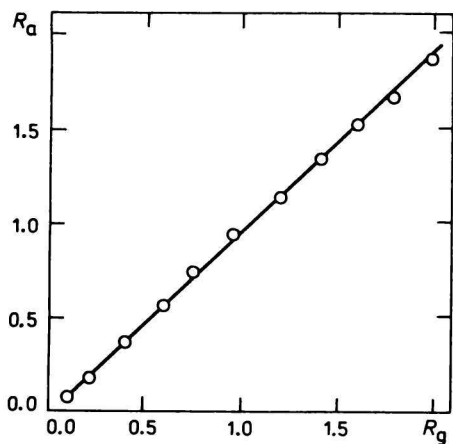

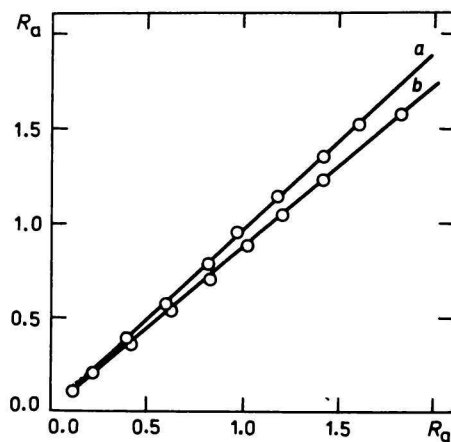*Fig. 4.* Analytical calibration curve of methyl methacrylate on Chromaton N Super with 10 % of FFAP.

Fig. 5. Analytical calibration curve of n-butyl alcohol (*a*) and butyl acrylate (*b*) on Chromaton N Super with 10 % of FFAP.

Table 2

Statistical processing of analytical calibration curves on Chromaton N Super with 10 % of FFAP

Characteristics	Methyl methacrylate (MMC)	n-Butyl alcohol (n-B)	Butyl acrylate (BAC)
Regression equation	$y = Kx$	$y = Kx$	$y = Kx$
Analytical constant (K)	0.933	0.925	0.898
Reliability interval of analytical constant (L_K)	0.933 ± 0.056	0.925 ± 0.048	0.898 ± 0.030
Reliability interval (L_{Ky}) of measured values $\{y\}$ as a function of values $\{x\}$	$0.933 \pm (3.9 \times 10^{-3} + \\ + 3.1 \times 10^{-3} \{x\}^2 - \\ - 6.2 \times 10^{-3} \{x\})^{1/2}$	$0.925 \pm (2.9 \times 10^{-3} + \\ + 2.3 \times 10^{-3} \{x\}^2 - \\ - 4.7 \times 10^{-3} \{x\})^{1/2}$	$0.898 \pm (1.4 \times 10^{-3} + \\ + 1.1 \times 10^{-3} \{x\}^2 - \\ - 2.2 \times 10^{-3} \{x\})^{1/2}$
Standard deviation ($s_{xy}K$) of scatter of calibration relation	0.036	0.032	0.022
Limit of determination x(lim)	$0.058 \text{ mmol dm}^{-3}$ $(5.8 \,\mu\text{g cm}^{-3})$	$0.070 \text{ mmol dm}^{-3}$ $(5.2 \,\mu\text{g cm}^{-3})$	$0.029 \text{ mmol dm}^{-3}$ $(3.7 \,\mu\text{g cm}^{-3})$

V. KOLLÁR, R. KEMKA, J. TÖLGYESSY

Table 3

Limit of determination

Substance	μ	$\bar{x}$	s	$L_{\bar{x}}$	s_r	$t_K(n-1; 0.05) = 2.5706$
			$\mu g\,cm^{-3}$		%	t
MMC	6.0	5.92	0.278	5.92 ± 0.29	4.7	0.7049
n-B	6.5	6.34	0.260	6.34 ± 0.27	4.1	1.5074
BAC	5.5	5.69	0.222	5.69 ± 0.23	3.9	2.0964

Table 4

Precision and accuracy of analysis of model samples

n	μ	$\bar{x}$	s	$L_{\bar{x}}$	s_r	$t_K(n-1; 0.05) = 2.5706$
			$\mu g\,cm^{-3}$		%	t
1	25.5	24.95	0.674	24.95 ± 0.71	2.7	1.9988
2	62.5	63.10	1.325	63.10 ± 1.39	2.1	1.1092
3	95.0	95.30	1.811	95.30 ± 1.90	1.9	0.4058
1	30.5	30.92	0.865	30.92 ± 0.91	2.8	1.1327
2	55.0	55.20	1.490	55.20 ± 1.56	2.7	0.3288
3	95.8	95.58	2.578	95.58 ± 2.71	2.7	0.2850
1	42.0	40.90	1.186	40.90 ± 1.24	2.9	2.2719
2	58.5	58.88	1.219	58.88 ± 1.13	2.1	0.7636
3	91.5	99.71	1.905	90.71 ± 1.99	2.1	1.0287

The calculated and experimentally verified values of the limit of determination correspond to $0.8\ mg\,m^{-3}$ concentrations of MMC, n-B, and BAC for sampling of $30\ dm^3$ of air.

Calculation of concentration of substances in atmosphere

The concentrations of MMC, n-B, and BAC in the analyzed air after sampling with a withdrawing tube were calculated from the amount of the substance captured on activated carbon and the quantity of taken air by means of the following formula

$$\varrho = \frac{R_a c_{i\text{-}B} k}{KV}$$

where the symbols ϱ, R_a, k, K, $c_{i\text{-B}}$, and V stand for average concentration of MMC, n-B or BAC in atmosphere ($\mathrm{mg\,m^{-3}}$), ratio of the area of chromatographic wave of MMC, n-B or BAC to the area of chromatographic wave of internal standard i-B, coefficient of dilution, analytical constant of the regression equation for MMC, n-B or BAC, concentration of internal standard i-B in extractive agent ($\mathrm{mg\,m^{-3}}$), and volume of the sampled air ($\mathrm{m^3}$), respectively.

The average concentration of chemical contaminants, *i.e.* MMC, n-B, and BAC after sampling with passive dosimeters was calculated by means of the formula

$$\varrho_t = 10^3 \frac{m_t}{DK_D t} \, \mathrm{mg\,m^{-3}}$$

where the symbols ϱ_t ($\mathrm{mg\,m^{-3}}$), m_t ($\mu\mathrm{g}$), t (s), D ($\mathrm{cm^2\,s^{-1}}$), and K_D (cm) stand for average mass concentration of the substance in air for time t, amount of the substance captured on solid sorbent in dosimeter in time interval t, exposure of dosimeter, diffusion coefficient of the substance, and constant of dosimeter, respectively.

The values of diffusion parameters of substances ascertained for two types of dosimeters in experimental testing in controlled atmosphere under defined conditions [10] are presented in Table 5.

Table 5

Values of diffusion parameters of substances

Substance	Diffusion parameter: $(DK_D)/(\mathrm{cm^3\,s^{-1}})$	
	Dosimeter $\check{\mathrm{K}}$	Dosimeter $\check{\mathrm{P}}$
MMC	0.251 ± 0.011	0.676 ± 0.011
n-B	0.250 ± 0.011	0.672 ± 0.009
BAC	0.224 ± 0.029	0.620 ± 0.054

Results and discussion

The developed method of determination of MMC, n-B, and BAC in working atmosphere consists in sampling of chemical contaminants with activated carbon, subsequent extraction of these substances, and gas chromatographic analysis. The conditions of gas chromatographic analysis were so optimalized that no interference of the determined substances with extractive agent took place in the course of their identification and determination.

Table 6

Equilibrium sorption power of the substances on activated carbon GA I (0.8—1.25 mm); volume flow of dry air 0.5 dm³ min⁻¹; temperature 293—298 K, pressure 101.5 kPa

Substance	Mass concentration of substance in air	Equilibrium sorption power
	mg m⁻³	mg g⁻¹
MMC	1600	187
n-B	800	237.7
BAC	1100	275

The experimental study of the equilibrium sorption power of activated carbon was carried out by the use of gravimetric method (Table 6). The break--through in the layer of activated carbon in withdrawing tubes was determined by estimating the input concentration (1 %—5 %) of the substance by gas chromatographic analysis. The results of experimental determination of the break-through in the layer of sorbent (activated carbon) are given in Table 7.

The optimum volume flow of the sucked air needed for concentrating the substances on activated carbon was determined under given conditions of sampling as a value under which no significant increase in time requisite for break-through appeared. The time of break-through is in relation to properties of the substances and is shorter at higher concentrations of the substances in air. No significant influence of water vapour on the time of break-through in activated carbon was observed at relative humidity of 35 %—52 %.

For dosimeter testing, the sorbent was exposed to constant testing concentration. The testing of a dosimeter in which the driving force is concentration gradient (difference between concentration at the entrance into dosimeter and concentration in interlayer of sorbent) takes place in the linear section of the isotherm of a given substance (the amount of the substance captured on sorbent in the time interval t is $m_t \ll m_{sat}$). The testing takes place under defined conditions in the region of low concentrations of sorbate, *i.e.* in the linear section of the isotherm of the substances. The model experiments with passive dosimeters have been described in papers [6, 10]. The linear relationship between quantity of the captured contaminants (m_t) and their concentration (ϱ) in exposure chamber is given in Fig. 6 for the exposure time t. The dosimeters were exposed in exposure chamber for 0.5—5 h. The atmosphere containing individual contaminants and their mixtures was continuously controlled by an infrared analyzer of gases and vapour MIRAN IA and gas chromatographic analysis. The concentration of contaminants varied in the range 12 mg m⁻³—850 mg m⁻³.

Table 7

Break-through in 300 mg layer of activated carbon in withdrawing tube; temperature 293—298 K, pressure 100.9—102 kPa, relative humidity 35—52 %

Substance	Mass concentration in air	Volume flow of air	m(Substance captured on carbon in withdrawing tube)/%		Break-through in carbon layer in the first withdrawing tube		
	$mg\ m^{-3}$	$dm^3\ min^{-1}$	in the first	in the second	after substance adsorption m/mg	after time t/min	after air sampling V/dm^3
MMC	50	0.2	97.6	2.4	1.8	180	36
		0.5	98.1	1.9	2.3	92	46
	250	0.2	98.1	1.1	8.6	170	34
		0.5	99.1	0.9	8.1	64	32
n-B	101	0.2	97.9	2.1	4.3	215	43
		0.5	96.8	3.2	4.1	82	41
	497	0.2	96.4	3.6	17.4	174	35
		0.5	95.9	4.1	15.3	61.2	30.5
BAC	50	0.2	99.4	0.6	3.3	330	66
		0.5	97.6	2.4	3.1	124	62
	246	0.2	97.8	2.2	11.8	240	48
		0.5	98.5	1.5	10.3	84	42

V. KOLLÁR, R. KEMKA, J. TÖLGYESSY

Fig. 6. Variation of quantity of the captured contaminant (m_t) with concentration of substances in atmosphere (ϱ) and exposure (t).
Dosimeter $\bar{K}$: a) MMC; b) n-B; c) BAC.
Dosimeter $\bar{P}$: a′) MMC; b′) n-B; c′) BAC.
○ MMC, n-B or BAC; ● mixture of substances.
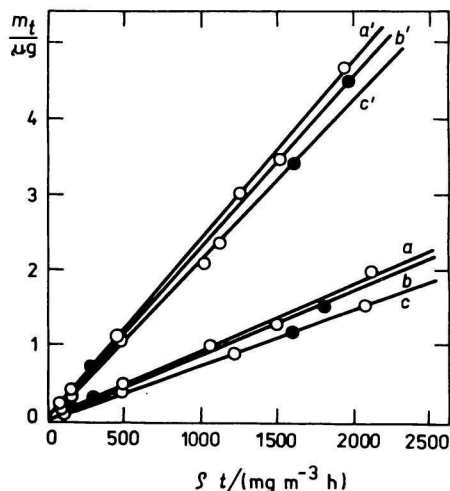
From the viewpoint of reliability, the optimum exposure of dosimeters must be so chosen that the dosimeter reacts upon external concentration of the substances. However, it is also necessary to take into consideration the losses due to reverse diffusion. This factor may be significantly effective in long-termed exposures or in case of varying concentration at the entrance into dosimeter. The values of losses are stated in paper [12] for the linear section of isotherms.

The accuracy and precision of determination is significantly affected by the efficiency of desorption. The recuperation of substances from the surface of activated carbon and the selection of convenient desorptive agent were studied by the method of phase equilibrium [13, 14]. The static extraction of the substances from activated carbon by carbon disulfide did not afford the required 95 % efficiency. The increase in polarity of carbon disulfide due to 5 volume % of isopropyl alcohol brought about the required efficiency of desorption (Table 8). The optimum time of static extraction was 50—60 min.

The separation of a mixture of substances in a column with 10 % of FFAP on Chromosorb W/AW or Chromaton N Super as stationary phase under the experimentally defined optimum conditions is to be characterized by the following resolution power of the column: $R = 1.71$ for MMC and i-B, $R = 1.29$ for i-B and n-B, and $R = 1.09$ for n-B and BAC. A variation of conditions of the chromatographic process involving programmed temperature increase in columns with 10 % of FFAP enables us to determine other esters of acrylic acid and methacrylic acid in the presence of each other as well as acrylic and methacrylic acid.

Table 8

Desorption efficiency and standard deviations of substances for $n = 6$; extractive agent: 5 % of isopropyl alcohol in carbon disulfide

A — dynamic method, B — direct dosage of substances on sorbent, C — dosage of substances in extractive agent on sorbent, D — method of phase equilibrium

Substance	Adsorbed mass	Desorption efficiency (DE/%) and standard deviation (s/%)							
	mg	A		B		C		D	
MMC	0.189	98.5	2.5	96.5	5.5	98.5	3.2	100.4	7.3
	0.378			97.1	8.2	97.9	1.2	99.8	4.3
	0.945	98.9	1.1	98.1	7.1	98.7	6.2	101.2	4.7
n-B	0.162	96.1	2.2	97.6	3.6	97.7	2.9	93.5	9.5
	0.324	96.7	5.3	95.5	9.5			98.2	7.3
	0.810	95.9	2.9	94.9	1.0	97.3	5.0	95.9	2.9
BAC	0.180			98.8	2.7	99.5	3.5	100.5	2.1
	0.360			97.7	2.3			99.7	5.9
	0.900	98.5	3.9	98.9	4.1	97.9	2.1	100.8	7.3
MMC		96.2	7.1	97.0	2.1	96.9	2.2	98.5	2.6
n-B	0.180	95.9	2.1	96.1	3.2	96.0	5.2	97.1	3.6
BAC (mixture)		97.2	4.3	97.9	9.8	98.1	2.1	99.2	3.9

Table 9

Results of field measurements in production of MMC; sampling by means of withdrawing tubes (T) and passive dosimeters ($\bar{K}$ and $\bar{P}$)

Sample	Exposure	Mass concentration of MMC/(mg m^{-3})			Relative error
	h	$\bar{K}$	$\bar{P}$	T	%
1	1	25.76	25.89	23.84	8.33
2	1	30.46	33.43	33.50	4.4
3	2	134.22	138.10	132.9	2.4
4	2	22.29	22.11	22.02	3.72
5	2	22.80	20.13	20.90	2.70
6	4	23.95	22.75	21.40	9.11

The presented method of determination of MMC, n-B, and BAC in working atmosphere fills a gap in analytical determination of these substances. It is appropriate for controlling and observing the admissible concentration of these substances as well as fixing the level of exposure of workers in their production and application. The method gives reliable results. Table 9 contains the results of field measurements of MMC in its production. It is evident that the results obtained by the use of stationary and personal sampling with passive dosimeters and withdrawing tubes are consistent provided equal conditions of sampling were respected.

References

1. Gronsberg, J. S., *Khim. Prom.* (Moscow) 7, 513 (1967).
2. Zurlo, N. and Motroco, L., *Medicina del Lavoro 51*, 241 (1960).
3. Gisolard, J. B., Robinson, D. B., and Kuno, P. J., *Amer. Ind. Hyg. Assoc. J. 19*, 43 (1958).
4. Vašák, V., *Chemická analýza pracovného ovzduší.* (Chemical Analysis of Working Atmosphere.) Státní zdravotnické nakladatelství. (State Publishing House of Public Health.) Prague, 1962.
5. Podkovyrina, N. Ts., Shumkova, L. A., and Tsybyshev, E. D., *Gig. Sanit. 5*, 61 (1982).
6. Kollár, V. and Kemka, R., *Bezpečná práca 14*, 65 (1983).
7. Czerczak, S., *Chem. Anal.* (Warsaw) *28*, 35 (1983).
8. Smolyar, N. Ya., *Gig. Sanit. 1*, 51 (1984).
9. Križan, J. (Editor), *Analýza ovzdušia.* (Analysis of Atmosphere.) Alfa Publishers, Bratislava, 1981.
10. Kollár, V., Kemka, R., and Tölgyessy, J., *Chem. Papers 41*, 235 (1987).
11. Waldman, M. and Vaněček, M., *Acta Hygienica Epidemiol. Microbiol.* (Institut hygieny a epidemiologie, Prague) *15*, 49 (1980).
12. Moore, G., Steinle, S., and Lefebre, M., *Amer. Ind. Hyg. Assoc. J. 45*, 145 (1984).
13. Domer, R. A. and Melcher, R. G., *Amer. Ind. Hyg. Assoc. J. 39*, 240 (1978).
14. Kaláb, P., *Chem. Listy 73*, 416 (1979).