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## Note

### Determination of volatile microimpurities in alkaline polymerizates and neutral propylene oxide polyethers by gas chromatographic headspace analysis

R. N. MOKEYEVA\*, Y. A. TSARFIN and W. ERNST

*Analytical Laboratory, All-Union Research Institute for Synthetic Resins, Vladimir (U.S.S.R.)*

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Headspace gas chromatography (GC) has been used to determine the level of volatile impurities in propylene oxide alkaline polymerizates<sup>1-3</sup>, enabling volatile products to be detected at contents within the range 0.001-0.0001%. Unlike direct chromatography, this procedure does not involve the use of solvent and avoids chromatographic column contamination with polymer moieties, while increasing the analytical sensitivity by two or three orders of magnitude.

The volatiles are determined by continuous gas extraction, resulting from the inert gas flow passing through the sample at a constant rate<sup>4-7</sup>. Two procedures are available:

(1) GC of the headspace over the polymerizate under steady-state conditions, with subsequent determination of the partition coefficient by continuous gas extraction;

(2) Dynamic method for discovering volatiles in the polymerizates based on the exponential decrease in the compound concentration in a vapour phase with gas extraction time, graphical calculation of its initial concentration in the vapour phase.

Both alternatives have been used in this study.

## EXPERIMENTAL

Headspace GC and calibration were carried out with a Tsvet-5 chromatograph, flame ionization detector and 3 × 0.03 m glass column packed with 20% bis(2-cyanoethoxy-2-methoxyethyl) ether on Chromosorb W (60-80 mesh), at 55°C and an argon flow-rate of 38 ml/min.

Fig. 1 shows an equilibrium vapour phase chromatogram of propylene oxide polymerizates.

The instrument was calibrated with standard solutions of the analysed components in dichloroethane or propanol within the concentration range of 0.25-0.50%; 1-2 ml of solution were injected into the evaporator.

Peak parameters were calculated from the chromatogram and the amount of compound per 1 cm<sup>2</sup> of peak area was found from

$$T = \frac{V_1 d c}{A \cdot 100} \text{ g/cm}^2 \text{ or g/cm} \quad (1)$$

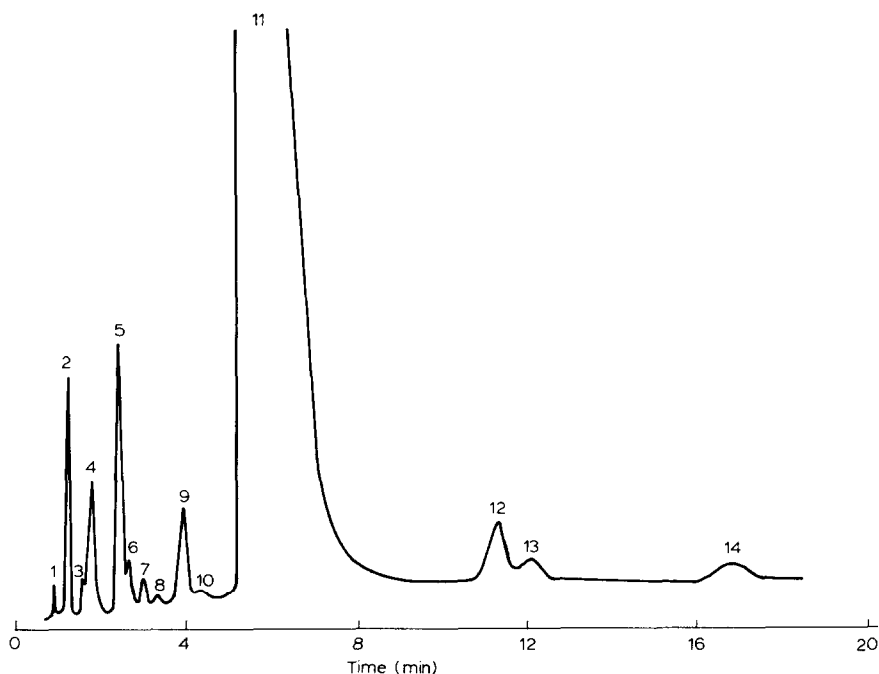


Fig. 1. Poly(propylene oxide) polyol gas phase chromatogram. Peaks: 1 = methane,  $4.3 \cdot 10^{-4}\%$ ; 2 = pentane,  $3.9 \cdot 10^{-4}\%$ ; 4 = hexane,  $5.4 \cdot 10^{-4}\%$ ; 5 = heptane,  $6.2 \cdot 10^{-4}\%$ ; 8 = ethylene oxide,  $0.2 \cdot 10^{-4}\%$ ; 10 = acetaldehyde,  $0.2 \cdot 10^{-4}\%$ ; 11 = propylene oxide, 5%; 12 = acetone,  $8.9 \cdot 10^{-4}\%$ ; 14 = isopropanol,  $4.3 \cdot 10^{-4}\%$ . 3,6,7,9,13 = unidentified components.

where  $V_1$  = injected volume (ml) of standard solution,  $d$  = solvent-specific gravity (g/ml),  $c$  = mass fraction (%) of analysed compound in standard solution, and  $A$  = parameter of chromatographic peak, area  $S$  (cm<sup>2</sup>) or height  $h$  (cm), of analysed compound.

In the static procedure (1) the equilibrium vapour phase was injected with a glass medical syringe (PTFE piston) which had been previously conditioned in an oven at 70°C. The determination of the partition coefficient of volatiles in the polymerizate-argon system by continuous gas extraction and in the dynamic procedure (2) was effected by injections into the equilibrium vapour phase using a six-way gas distribution tap with a 1-ml loop. To avoid sorption and condensation of volatiles in the injector, supply lines and loop, the entire injection unit was maintained at 120°C in the chromatograph-detector thermostat (the electron-capture detector having been removed). The apparatus for thermostating the samples and continuous gas extraction was supported over the thermostat containing the injection unit. It was closed with a silicone rubber plug and connected to the injector with a stainless-steel welded needle point capillary.

Due to the pronounced effect of temperature on the distribution of compounds between heterogeneous phases, the samples were conditioned in a water thermostat with an accuracy of  $\pm 0.1^\circ\text{C}$ .

The optimal sample thermostating temperature varies with the nature of the

temperature dependence of the partition coefficient and with the stability of the system to be analyzed. The most suitable temperature for propylene oxide alkaline polymerizates was found to be 50°C at which samples thermostatted for 2–3 h brought about no appreciable change in compound concentration in the equilibrium vapour phase due to possible reactions with the alkaline medium. At 50°C, thermodynamic equilibrium in the polymerizate-argon system is attained within 15–30 min, as evidenced by the constancy of the analyzed compound concentration in the gas phase (see Fig. 2).

To determine volatile microimpurities in the propylene oxide polymerizates by the first procedure (1), up to 4.000 g of sample were placed in a 50-ml water-jacketed sample thermostating vial which was then closed with a silicone rubber plug connected to a water thermostat and thermostatted at 50°C for 30 min.

The peak areas of the analysed components were calculated from the chromatogram of the equilibrium vapour phase sampled by a medical syringe,  $V$  ml, and the compound concentration in the gas phase was determined from:

$$C_g = T S/V \text{ g/ml} \quad (2)$$

The partition coefficients of the components in the propylene oxide polymerizate-argon system were determined by continuous gas extraction using previously prepared compound-polymerizate mixtures within the concentration range of 0.001–0.01%. A 4-g amount of the mixture was placed in a 20-ml water-jacketed gas extraction vessel which then was connected to the water thermostat preheated at 50°C and through a welded metal needle capillary to the injection unit. Gas sampling was started 5 min after gas extraction commenced and was carried on until the peak area had changed two- or three-fold. It was timed to fit the compound retention times and the partition coefficient values.

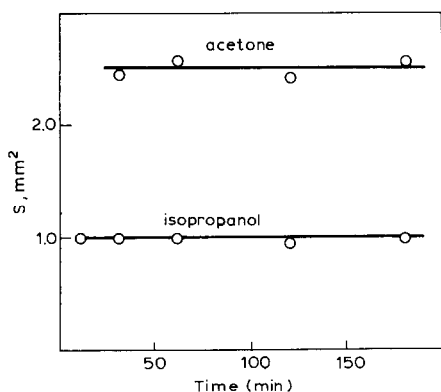


Fig. 2. Stabilization of acetone and isopropanol equilibrium concentrations in the alkaline polymerizate-argon system at 50°C.  $S$  = Peak area ( $\text{mm}^2$ ).

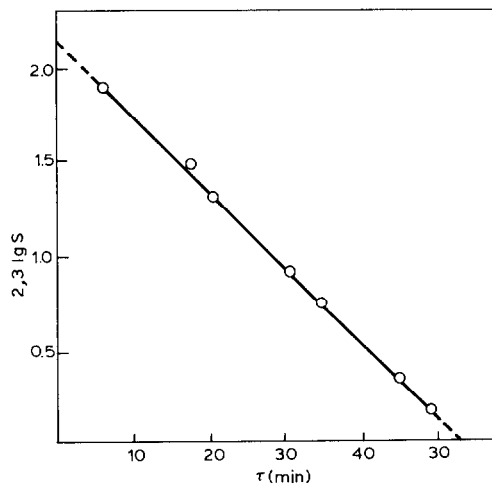


Fig. 3. Acetone peak area as a function of the duration of argon flow through the propylene oxide polymerizate. Thermostating temperature: 50°C;  $\nu = 16.27$  ml/min;  $V_1 = 4.27$  ml.

The partition coefficients,  $K$ , were calculated from<sup>8</sup>

$$K = \frac{\tilde{v} (t_n - t_1)}{\ln \frac{S_1}{S_n} \cdot V_1} \quad (3)$$

where  $\tilde{v}$  = gas flow-rate (ml/min),  $t_1$ ,  $t_n$  = times (min) of the first and  $n$ th gas extraction samplings,  $S_1$ ,  $S_n$  = peak areas of analysed compounds in the first and  $n$ th samplings and  $V_1$  = volume (ml) of the polymerizate analysed. At least four samples were taken and the average partition coefficient calculated from three parallel equations.

The contents of the compounds in the propylene oxide alkaline polymerizate,  $C_1^0$ , was found using the observed values of  $C_g$  and  $K$

$$C_1^0 = C_g \left( K + \frac{V_g}{V_1} \right) \quad (4)$$

where  $V_g$  is equilibrium gas phase volume.

In the dynamic approach (2), 4.000 g of the polymerizate were placed in a 20-ml gas extraction vessel maintained at 50°C. As in the case of the partition coefficient determination, sampling was performed 5 min after gas extraction had begun by means of an injector. The time intervals between injections were set in accordance with the retention time of the last peak. At least four gas extract samples were taken. Peak areas were calculated from the chromatograms obtained, and the value corresponding to the concentration of the component in the gas phase,  $C_g^0$ , at time  $\tau = 0$  min (Fig. 3), found by extrapolating the curve  $\ln S = f(\tau)$  onto the  $y$  axis.

The content of an analysed compound in a sample was determined from

$$C_1^0 = C_g^0 \tilde{v} / \beta V_1 \quad (5)$$

where  $\beta$  is the slope of the curve  $\ln S = f(\tau)$ .

## RESULTS AND DISCUSSION

Eqn. 5 for the calculation of the content of volatiles in a non-volatile liquid (polymerizate) may be obtained from the relationship describing the decrease in content of volatiles in a solution as a result of an inert gas being passed through it at a constant rate,  $v$  (ref. 4)

$$\ln \frac{C_1^0}{C_1} = \frac{V_{gf}}{KV_1} \quad (6)$$

where  $V_{gf}$  = volume of gas flow during the time  $\tau$ . Using the relationships  $C_1 = KC_g$ ,  $V_{gf} = \tilde{v}\tau$  and eqn. 2 at  $v = 1$ , eqn. 6 can be rewritten as:

$$\ln S = \ln \frac{C_1^0}{KT} - \frac{\tilde{v}}{KV_1} \cdot \tau \quad (7)$$

Eqn. 7 is linear and represents the peak area of the compound in the gas phase as a function of the gas extraction time,  $\tau$ . Its slope  $\beta = \tilde{v}/KV_1$ , hence:

$$K = \tilde{v}/\beta V_1 \quad (8)$$

With  $\tau = 0$ , eqn. 7 assumes the form:

$$S^0 = C_1^0/KT \quad (9)$$

Eqn. 5 may be inferred from eqns. 8 and 9:

$$C_1^0 = \frac{S^0 T \tilde{v}}{\beta V_1} = \frac{C_g^0 \tilde{v}}{\beta V_1}$$

The results obtained for the determination of the acetone content in alkaline polymerizates using eqn. 5 were compared (Table I) with those calculated from the equation suggested in ref. 4:

$$C_1^0 = C_g \cdot \frac{V_g - V_g^0}{V_1 \cdot \ln \frac{A_g^0}{A_g}} \cdot \exp \left[ \frac{V_g^0 \cdot \ln \frac{A_g^0}{A_g}}{V_g - V_g^0} \right] \quad (10)$$

It is noteworthy that eqn. 10 describes the continuous gas extraction model where the analysed compound is backflushed under the conditions of thermodynamic equilibrium between phases. In other words, as a gas bubble passes through a liquid layer, instantaneous exchange occurs not only between its volume and solution but also between above-the-liquid-surface volume and solution. Therefore, both the ex-solution bubble and the above-the-solution gas have equal concentrations of analysed compound<sup>5</sup>.

The good agreement between the results calculated from eqns. 5 and 10 demonstrates the validity of eqn. 5. It also proves that the backflushing of volatiles from

TABLE I  
ACETONE ANALYSIS IN PROPYLENE OXIDE ALKALINE POLYMERIZATES

$C \cdot 10^{-5} \text{ (g/ml)}$	
Eqn. 5	Eqn. 10
9.37	9.35
29.09	29.49
42.73	42.28
36.08	37.36
23.28	23.40
23.84	23.90

TABLE II

PRODUCT  $C_g^i \bar{v}^i$  FOR ACETONE AS A FUNCTION OF GAS FLOW-RATE IN THE ALKALINE POLYMERIZATE-ARGON SYSTEM

$\bar{v}^i$ (ml/min)	15	15.4	20.2	23	26	29.5	33	40.2	51	56
$C_g^i \cdot 10^{-7}$ (g/min)	13	12.5	13.0	12.5	12.7	13.0	12	12.6	13.5	12.5

propylene oxide polymerizates by the inert gas (argon) flow was carried out under thermodynamic equilibrium at all stages.

In this case loss of compound from the solution proceeds exponentially, and the concentration of a compound in the gas phase before the start of gas extraction (at  $\tau = 0$ ) coincides with the maximum compound concentration in the gas phase. It enables the value of  $\ln S^0$  (hence  $C_g^0$ ) to be found by extrapolating  $\ln S = f(\tau)$  onto the  $y$  axis at a preselected gas flow-rate.

According to our experimental data, the range of inert gas flow-rate which ensures maintenance of thermodynamic equilibrium is 15–60 ml/min. In this range the product  $C_g^i \bar{v}^i$  is constant irrespective of gas flow-rate (see Table II). Here  $C_g^i$  and  $\bar{v}^i$  are respectively the compound concentration in the gas phase and gas flow-rate at the time  $i$ .

The selection of which procedure to adopt depends on the content and qualitative composition of the impurities. When the content of impurities borders on the limit of sensitivity of the method it is useful to follow the first procedure (1), combining equilibrium vapour sampling with the dynamic analysis of partition coefficients in model mixtures of compounds in the polymerizates investigated. Should the amount of compound be sufficient for four gas phase extractions, it is advisable to resort to the second procedure (2), *i.e.*, continuous gas extraction.

Table III gives the results of volatiles analysis in propylene oxide polymerizates as well as the partition coefficients and mean-square errors,  $S$ .

The procedures suggested may also be used for analysis of neutral propylene oxide polyethers.

TABLE III

ANALYTICAL DATA FOR PROPYLENE OXIDE ALKALINE POLYMERIZATE AND POLYMERIZATE-ARGON SYSTEM PARTITION COEFFICIENTS AT 50°C

Compound	$C \cdot 10^{-4}$ (%)	$S \cdot 10^{-4}$ ( $n = 8, r = 0.95$ )	$K$	$S$ ( $n = 10, r = 0.95$ )
Methane	4.3	0.4	5.75	0.10
Pentane	3.9	0.2	47.2	2.6
Hexane	5.4	0.9	78.2	2.3
Heptane	6.2	0.7	159.8	4.6
Ethylene oxide	0.2	0.02	23.8	1.2
Propylene oxide	—	—	61.0	1.4
Acetaldehyde	0.2	0.04	36.8	0.5
Propionaldehyde	—	—	46.6	2.2
Acetone	8.9	0.6	79.9	2.1
Isopropanol	4.3	0.3	60.4	2.6

## CONCLUSIONS

To determine the content of methane, pentane, hexane, heptane, ethylene oxide, propylene oxide, acetic and propionic aldehydes, acetone and isopropanol microimpurities in propylene oxide polymerizates, two procedures have been proposed: static head space analysis with determination of partition coefficients by continuous gas extraction and continuous gas extraction analysis. For the latter we have suggested an equation and a method for the determination of the initial equilibrium concentration of the analysed compound in a gas phase by extrapolation of the curve  $\ln S = f(\tau)$ .

Thermodynamic equilibrium has been shown to be maintained in the gas extraction analysis of microimpurities in propylene oxide alkaline polymerizates within the flow-rate range of 15–60 ml/min.

Partition coefficients have been determined for microimpurities in the polymerizate-argon system.

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