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PURITY CONTROL OF CAPROLACTAM BY HEAD-SPACE GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The head-space sampling technique, in combination with gas–liquid chromatography (GLC) on superficially bonded (Carbowax 20M) packings, is proposed for the purity control of caprolactam. To determine the content of impurities in the original sample from its vapour-phase chromatogram, the conventional procedure of internal normalization has been modified by introducing appropriate conversion factors instead of the commonly used peak-area correction coefficients. A suitable procedure for determining the conversion factors has been developed. The application of GLC head-space analysis to industrial purity control of caprolactam is illustrated by samples obtained from a Bulgarian chemical plant.

INTRODUCTION

Caprolactam is a monomer mainly used as a raw material in the production of both Nylon 6 and polyamide fibre. The purity requirements in such processes are very strict because of the direct influence of impurities on the polymerization as well as on the properties of the fibre produced. The industrial production of caprolactam is realized on the basis of several schemes, the most common process employed being the Beckmann rearrangement of cyclohexanone oxime, obtained from cyclohexanone.

The impurities in caprolactam originate from the raw materials used in its syntheses, from side reactions and especially from the oxidation of caprolactam owing to its high sensitivity to oxygen[1,2]. The main problems in determining these impurities are due to their great variety and low concentrations. This is why the common methods of caprolactam purity control in industry are non-specific, *e.g.*, evaluation of alkalinity, acidity and permanganate number, allowing the determination of only some classes of impurities.

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An especially effective tool for the total determination of the caprolactam impurities appears to be gas–liquid chromatography (GLC)[3–8]. Together with mass spectrometry or infrared spectroscopy, it enables both the identification and the quantitation of impurities present in the monomer. For the purposes of industrial production, however, it is usually enough to determine only the concentration of the impurities, while their identification is largely of scientific interest. One of the main problems in the GLC analysis of impurities is connected with the need for appropriate sampling techniques, enabling the injection of an adequate amount of monomer into the column. This is important not only for detecting the impurities present at low concentrations, but also for reducing the so-called "memory" effect, observed with conventional Carbowax 20M column packings[3,5–7] and causing deterioration in the separation and quantitation.

Two main approaches have been proposed to overcome the sampling problem: injection of a concentrated (50%, w/w) monomer solution and injection of molten monomer[3–8]. However, there are several disadvantages in applying these techniques: *e.g.*, in the case of a monomer solution, (1) the need for solvents of ultra-high purity, (2) a large tailing solvent peak, often interfering with the small impurity peaks in the chromatogram; in the case of a molten monomer, (3) loss of some volatile impurities while melting the monomer, (4) partial oxidation of caprolactam, thus leading to generation of new impurities, (5) blockage of the syringe needle or even damage to the syringe, (6) overloading the column, resulting in low efficiency and a strong "memory" effect.

No comments have been published on the memory effect, which is observed with conventional column packings. Due to sample overload and/or strong interfacial adsorption phenomena, the "memory" effect results in a permanent baseline drift under isothermal conditions or in a "ghost" chromatogram in a blank temperature-programmed experiment. This problem causes significant difficulties when the GLC technique is applied to the purity control of caprolactam.

In the present paper, the head-space sampling technique is proposed, together with so-called superficially bonded packings for GLC separation of caprolactam impurities. This approach offers many advantages, which, together with the simple quantitation procedure described, enable the application of GLC to the industrial purity control of caprolactam.

EXPERIMENTAL

Apparatus

A Model 419 gas chromatograph (Packard Instrument, Delft, The Netherlands) with a dual column system and a dual flame ionization detector was used for chromatographic separations, in combination with a laboratory-built head-space device for six sample vials. Chromatograms were registered by a 1-mV, Model 194 electronic recorder (Honeywell, Newhouse, U.K.) in combination with a Model M2 calculating integrator (Perkin-Elmer, Norwalk, CT, U.S.A.). All separations were performed on standard Pyrex glass columns, 1 m × 3 mm I.D.

Materials

Celite 545 (BDH, Poole, U.K.), 80–100 mesh, and Carbowax 20M (Carlo Erba,

Milan, Italy) were used for preparation of column packings. Caprolactam samples were obtained from a chemical plant in Stara Zagora, Bulgaria. Argon of 99.99% purity was employed as carrier gas.

Procedures

Superficially bonded packings were prepared with 1.5% Carbowax 20M on Celite 545 as described previously[9,10]. For the preparation of samples, 2 g caprolactam were weighed in a 6-ml glass vial and sealed in an argon atmosphere with an aluminium-faced silicone septum. For all separations, 0.5-ml vapour samples were injected into the column.

Chromatographic conditions

Separations were carried out by temperature programming from 60 to 220°C at 5°C/min. The initial and final isotherms were 1 and 9 min, respectively. The injectors and detectors were heated at 220°C. Optimum flow-rates were as follows: carrier gas, 10 ml/min; hydrogen, 20 ml/min; air, 200 ml/min.

Head-space conditions

All samples were equilibrated for at least 2 h at 150°C. The temperature was controlled electronically and maintained constant within ±0.1°C.

RESULTS AND DISCUSSION

Head-space technique for caprolactam sampling in GLC

The head-space technique is commonly used in GLC for separating low-level volatile substances, present in polymers or other non-volatile or poorly volatile materials. An important advantage of its application appears to be the protection of the column from undesirasble compounds which can cause irreversible changes in packing efficiency or even block the column. However, for caprolactam sampling in GLC, it is impossible to prevent the injection of its vapour into the column. Usually, there are, in addition to some volatile impurities, also substances having volatility comparable with that of caprolactam itself. Hence, a higher temperature than that in conventional head-space applications is necessary to equilibrate the vapour phase with the molten caprolactam. According to our experience, good results can be obtained at 150°C in no more than 2 h of equilibration. Then, the vapour sample injected contains all of the components present in the liquid phase. To prevent possible oxidation of caprolactam during the equilibration, the void volume of the vial employed must be flushed by an inert gas, *e.g.*, argon or nitrogen.

The main advantages in applying the head-space technique for caprolactam sampling are: (1) no need for ultra-pure solvents for sample preparation; (2) direct vapour injection into the column; (3) the vapour sample is enriched with most of the volatile impurities; (4) no danger of oxidation; (5) no danger of sample overload.

In fact, sawmple overload is an important factor in the "memory" effect of the column. In an effort to solve this problem, we have found the properties of the column packing itself to be crucial. It is necessary to minimize, first, the possibility of adsorption of some substances at the interphase boundaries in the packing. Secondly, a small amount of liquid stationary phase must be used to facilitate dif-

fusion, which helps to increase the efficiency of the column. Both effects are easily achieved with the so-called superficially bonded (Carbowax 20M) packings, prepared according to the recommendations of Aue and Hastings[9,10]. Their main advantages are: (1) high thermal stability, allowing temperature programming in GLC; (2) no/or only minimum "memory" effect in the case of sample overload; (3) high separation efficiency at relatively short retention times.

Problems of quantitation

The application of the head-space sampling technique to the GLC purity control of caprolactam allows in principle the quantitation of impurities in the vapour phase of the sample. To this end, it is necessary to employ a suitable procedure for quantitative interpretation of the chromatograms obtained. However, it is more important to know the concentration of impurities in the liquid caprolactam itself. The vapour/liquid-phase equilibration in the vial changes both phase compositions as compared to those of the original caprolactam sample. Hence, two main problems arise with the quantitation: (1) selection of a convenient procedure of chromatogram acquisition and (2) derivation of appropriate correction factors for the peak areas that enable calculation of the original sample content from the chromatogram of the vapour phase.

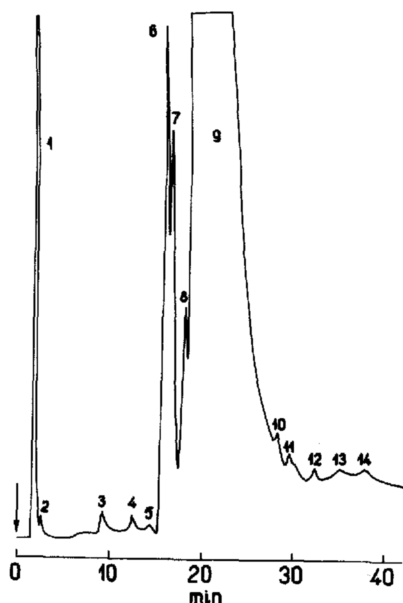
With the peculiarities of the analytical task in mind, we have employed the procedure of internal normalization for quantitation of the chromatograms. It was suitably modified to permit the application of so-called conversion factors instead of the commonly used peak-area correction coefficients. An appropriate procedure for calculating these factors was developed as described below.

Procedure for determining the conversion factors

An appropriate caprolactam sample is required, containing most of the possible impurities, which is then processed under the same head-space and chromatographic conditions as recommended above. As shown in Fig. 1, a chromatogram of the sample vapour phase is obtained, in which all peaks of the impurities (peaks 1–8 and 10–14) and caprolactam (peak 9) itself are recorded. The sample is taken before the final industrial purification step. Further, an additional chromatogram of the original sample must be obtained (Fig. 2) by injecting molten caprolactam into the column. To this end, a glass vial is completely packed with the sample, so that in the molten state the liquid fills the entire volume of the vial. The vial is then sealed with an aluminium-faced silicone septum and thermostatted at 90°C.

Now, let us assume that n peaks (including that of caprolactam) are recorded in each of two chromatograms obtained from the liquid and the vapour samples. Also, that peaks having identical retention times correspond to a single substance or to a few unseparated substances, present as impurities in the caprolactam sample. The peak areas of the ith component in the liquid and the vapour samples, are denoted as A_i^L and A_i^V respectively. Then, the percentage, P_i, of the ith component in both samples can be expressed as

$$P_i^L = 100 q_i A_i^L / \sum_{j=1}^{n} q_j A_j^L \qquad (1)$$



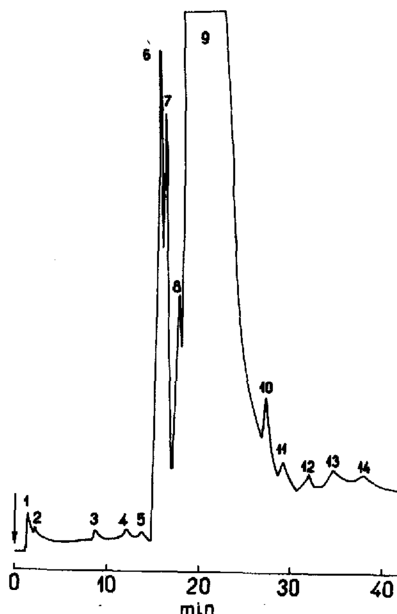


Fig. 1. Head-space chromatogram of a caprolactam sample (vapour phase) prior to final purification. Peaks: 1–8 = impurities, 9 = caprolactam, 10–14 = impurities.

Fig. 2. Chromatogram of a melt of the same sample as in Fig. 1. Peaks as in Fig. 1.

and

$$P_i^V = 100q_iA_i^V/\sum_{j=1}^{n} q_jA_j^V \tag{2}$$

where q_i are the corresponding peak-area correction coefficients for the components (i = 1, 2, ..., n).

It is evident that, under a constaqnt head-space and chromatographic conditions for each sample component, the ratio of P^L to P^V will be a constant, k, the value of which is dependent on the saturated vapour pressure of the component. Then, taking into account eqns. 1 and 2, we can write

$$k_i = P_i^L/P_i^V = A_i^L \sum_{j=1}^{n} q_jA_j^V/A_i^V \sum_{j=1}^{n} q_jA_j^L \tag{3}$$

where k_i represent the necessary conversion factors. Obviously, eqn. 3 can be used for accurate evaluation of the factors only in cases where the corresponding q values are known. As it is difficult to find relevant data in the literature or to determine them experimentally, we simplified eqn. 3 as follows.

It is clear that nearly 99% (or even more) of each $\sum_j q_jA_j^s$ value (s = L or V)

represents the areas of the caprolactam peaks, *i.e.*, A_c^L and A_c^V, respectively. Hence, we can assume the following relationships to be valid

$$\sum_{j=1}^{n} q_j A_j^L \approx \lambda A_c^L \quad \text{and} \quad \sum_{j=1}^{n} q_j A_j^V \approx \lambda A_c^V \tag{4}$$

where λ is a proportionality parameter. Combining eqn. 4 with eqn. 3, we obtain

$$k_i = A_i^L A_c^V / A_i^V A_c^L \tag{5}$$

which enables an approximate estimation of the conversion factors. It is impoortant to point out that k for caprolactam is always unity. The conversion factors are presented in the second column of Table I. They are the mean values from three determinations. Having these at our disposal, it is necessary only to obtain the chromatogram of the vapour sample and the corresponding values of the peak areas, A_i. The latter are related to the separated components, their percentages, P_i, being determined from

$$P_i = 100 k_i A_i / \sum_{j=1}^{m} k_j A_j \tag{6}$$

TABLE I

CONVERSION FACTORS AND CONTENTS OF IMPURITIES IN DIFFERENT CAPROLACTAM BATCHES, DETERMINED BY HEAD-SPACE GLC

Peak No.	*Conversion factor**	*Caprolactam batch***			
		1	*2*	*3*	*4*
1	0.0386	$3.91 \cdot 10^{-4}$	$7.64 \cdot 10^{-4}$	$1.40 \cdot 10^{-4}$	$4.16 \cdot 10^{-3}$
2	0.833	–	–	$1.21 \cdot 10^{-4}$	–
3	0.403	–	–	–	–
4	0.865	$4.70 \cdot 10^{-3}$	$2.86 \cdot 10^{-3}$	–	–
5	0.970	$5.00 \cdot 10^{-3}$	$5.70 \cdot 10^{-3}$	$5.17 \cdot 10^{-4}$	–
6	0.814	$6.34 \cdot 10^{-3}$	$2.57 \cdot 10^{-2}$	$1.08 \cdot 10^{-2}$	$2.55 \cdot 10^{-2}$
7	0.948	$3.52 \cdot 10^{-3}$	$2.15 \cdot 10^{-2}$	$8.05 \cdot 10^{-3}$	$1.81 \cdot 10^{-2}$
8	0.932	$1.54 \cdot 10^{-2}$	$4.28 \cdot 10^{-2}$	$1.48 \cdot 10^{-2}$	–
9***	1.00	99.96	99.88	99.95	99.93
10	2.48	–	$7.12 \cdot 10^{-3}$	$1.17 \cdot 10^{-2}$	$5.90 \cdot 10^{-3}$
11	0.964	–	$6.58 \cdot 10^{-3}$	$8.47 \cdot 10^{-4}$	$1.42 \cdot 10^{-2}$
12	1.04	–	$3.72 \cdot 10^{-3}$	–	$1.61 \cdot 10^{-3}$
13	1.11	–	$9.62 \cdot 10^{-4}$	–	–
14	1.19	–	–	–	–

* Values are reliable if the total concentration of impurities does not exceed 1%.

** Standard deviations vary from batch to batch: 1, from $\pm 3.1 \cdot 10^{-5}$ to $\pm$ $7.6 \cdot 10^{-5}$; 2. from $\pm 9.7 \cdot 10^{-6}$ to $\pm 6.9 \cdot 10^{-5}$; 3, from $\pm 2.6 \cdot 10^{-5}$ to $\pm 8.3 \cdot 10^{-5}$; 4, from $\pm 1.8 \cdot 10^{-5}$ to $\pm 7.4 \cdot 10^{-5}$.

*** Caprolactam.

where $m \leqslant n$ is the total number of components in the caprolactam sample analyzed. Hence, eqn. 6 permits the internal normalization to be used for direct quantitation of the caprolactam impurities by head-space GLC.

The percentages of the impurities in four batches of purified caprolactam are also given in Table I (columns 3–6), as the mean values from three determinations. Although different impurities are detected in different samples, their total concentration is approximately the same (0.05%), except for batch 2, where the concentration was 0.12%.

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