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Examination of organic trace contamination and thermo-oxidative deterioration of ε-caprolactam by high-performance liquid chromatography

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SUMMARY

Technical ε-caprolactam, used in the manufacture of polyamides, can be examined using high-performance liquid chromatography on silica gel with acetonitrile as the mobile phase and UV detection at 200 nm in order to determine organic impurities that affect the quality of the final product. A linear correlation was found between the adipimide content of the caprolactam samples, which acts as a measure of their deterioration by oxidation, and the quality index "volatile basis" and also between the aniline content and the so-called "permanganate extinction number". On the basis of the proposed method, a thermo-oxidation value can be defined.

INTRODUCTION

ε-Caprolactam is an important starting material in the production of polyamides (Dederon, Perlon L, nylon 6, etc.). However, certain organic impurities in monomeric ε-caprolactam reduce the quality of the final products[1,2]. Partial thermo-oxidative reaction of ε-caprolactam during processing, storage and transport can also occur forming oxidation products that have an adverse effect on the quality of the polymerizate and the polyamide fibres (*e.g.*, chain breakage, discoloration, embrittlement).

Chemical characteristics are commonly determined, *e.g.*, "permanganate extinction number", "UV extinction" and "volatile bases"[3].

For the determination of the permanganate extinction number (PEZ), according to ref. 3, 20 g of caprolactam are dissolved in 25 ml of 0.5 *M* sulphuric acid and treated with 1.00 ml of 0.02 *M* potassium permanganate solution at 25.0 ± 0.5°C. The extinction *E* at 545 nm is determined after 600 s, and the permanganate extinction number is calculated as PEZ = $Ef \cdot 100$, where *f* is the factor of the photometer correction[3]. To determine the so-called volatile bases according to ref. 3, 20 g caprolactam are dissolved in 100 ml of distilled water and 100 ml of 1 *M* sodium hydroxide solution are added. By means of a special distillation assembly[3], 10 ml of the solution are distilled into a calibrated vessel containing 10 ml of 0.01 *M* hydrochloric

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acid, 100 ml of distilled water and 5 droplets of methyl red–methylene blue indicator mixture. The excess of the acid is titrated with 0.01 *M* sodium hydroxide and corrected by a blank. The base number can be calculated as mequiv./kg. However, in view of the above, the determination of individual impurities in ε-caprolactam is clearly of major importance.

Chromatographic methods are particularly useful in identifying and determining organic impurities in ε-caprolactam, and especially gas chromatography has often been applied[4–15]. However, high-performance liquid chromatography (HPLC) is in principle more promising for less volatile substances[16]. So far HPLC has only been used to separate and identify cyclic oligomers of ε-caprolactam[17,18], and there has also been a report on the determination of ε-caprolactam and its metabolites using HPLC[19].

The aim of this paper is to show the possibilities of using HPLC for determining organic trace impurities in technical ε-caprolactam. We mainly examined the determination of aniline (the origin of which is discussed in ref. 20), cyclohexanone oxime and adipimide. The last compound should also allow the determination of the oxidative deterioration of ε-caprolactam.

EXPERIMENTAL

Equipment

A Hewlett-Packard HP 1090 M liquid chromatography system with a diode-array detector and an 7999 A HPLC workstation, consisting of an HP 310 computer, HP 9153 A Winchester disc drive, HP 2225 A ink-jet printer and HP 7440 plotter, was used.

Solvents

Water was distilled and filtered over a G-4 frit prior to chromatography. Acetonitrile, extra pure for UV spectroscopy (PCK, Schwedt, G.D.R.) with a water content of 0.35% (w/w) was used.

Test substances, calibration solution and test mixture

The purity of the test substances used was determined by liquid chromatography.

A stock solution of 7 mg of aniline, 42 mg of cyclohexanone oxime, 13 mg of adipimide and 50 mg of octahydrophenazine in 100 ml of acetonitrile was used for the determination of individual components. The stock solution was diluted 1:100 to give a working standard solution.

The chromatographic separation system was optimized using a test mixture of 40 mg of aniline, 65 mg of cyclohexanone oxime, 34 mg of adipimide, 70 mg of octahydrophenazine, 65 mg of *n*-valeramide, 25 mg of ε-methylcaprolactam, 250 mg of N-methylcaprolactam, 300 mg of acetamide and 120 mg of ε-caprolactam in 100 ml of acetonitrile.

Samples

Original samples from various caprolactam manufacturers and also oxygen-impaired products prepared by aeration of pure molten caprolactam at 100°C were used as solutions of 10 g of sample in 25 ml of acetonitrile.

Chromatographic conditions

The separation columns were each 200 mm × 2 mm I.D., containing ES-Gel 10 spherical silica (4 μm) from Leuna-Werke (Leuna, G.D.R.). The column filling was prepared by the balanced-density technique with dioxane and 1,2-dibromoethane. The mobile phase[a] was acetonitrile–water (99:1, v/v) at a flow-rate of 0.42 ml/min. The column temperature was 40°C, detection wavelength 200 nm (band width 4 nm), reference wavelength 550 nm (band width 100 nm) and injection volume 2 μl (*ca.* 800 μg of sample substance).

RESULTS AND DISCUSSION

Determination of a suitable separation system

At the start of the experiments reversed-phase (RP) systems were tested for their suitability for the determination of impurities in caprolactam, based on RP-8 and RP-18 materials with aqueous–organic mobile phases. The retention properties of the test substances demonstrated the general suitability of such systems. In this manner, for example, the adipimide from the thermo-oxidation of ε-caprolactam is eluted before the main component ε-caprolactam and can be determined using an RP-8 column (200 × 4.6 mm I.D.) and methanol–water (65:15 v/v) as the mobile phase with a detection wavelength of 205 nm. However, the disadvantage of this system is that some quality-affecting impurities, *e.g.*, aniline and cyclohexanone oxime, are eluted after the main component, which results in non-optimum conditions for the determination of trace amounts.

The separation problem was solved by using silica gel and acetonitrile, with which all the test substances examined eluted before the caprolactam peak. The addition of *ca.* 1% of water to the acetonitrile was found to improve the chromatographic resolution and analysis time (Fig. 1). A further decrease in the water content (*e.g.*, down to 0.1%) prolonged the analysis time. Occasionally, this can be advantageous because changes in selectivity also occur. The retention values show good reproducibility (relative standard deviation, R.S.D. = 0.5%).

The excellent separation selectivity of the chosen system is shown by the chromatogram of a test mixture of possible caprolactam impurities in Fig. 2. Table I gives the overall retention times (t_R) of several test substances. Some compounds cannot be separated from each other. Aniline and cyclohexanone, for example, are eluted together. Because of the considerably smaller molar absorptivity of cyclohexanone ($\varepsilon_{200} \approx 40$ l mol^{-1} cm^{-1}) compared with that of aniline ($\varepsilon_{200} \approx 31\,000$ l mol^{-1} cm^{-1}), the determination of aniline is only affected at a large excess of cyclohexanone, which is not to be expected in pure caprolactam.

Examination of caprolactam samples

Fig. 3 shows the chromatogram of ε-caprolactam with a serious deterioration of quality and a permanganate extinction number of zero. The size of the aniline peak should be noted. Cyclohexanone oxime and adipimide were identified as further

[a] Contrary to the internationally accepted nomenclature, which is followed in the *Journal of Chromatography*, the authors prefer the terms "compact phase" and "fluid phase", which correspond to the accepted terms "stationary phase" and "mobile phase", respectively. They feel that the former are generally applicable because the "stationary phase"is not always stationary but is moving during some well-known chromatographic processes, whereas the "mobile phase" does not have to be moved to realize the chromatographic phenomenon[30]. For further information, see ref. 31.

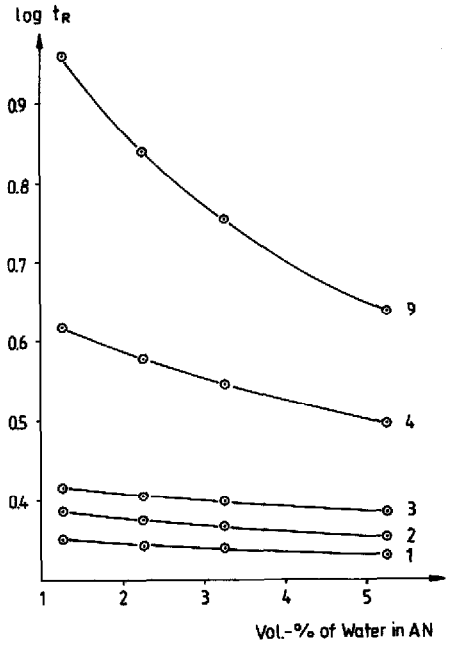


Fig. 1. Influence of the water content of acetonitrile on the overall retention time, t_R, of selected compounds. Conditions: stationary phase, Es-Gel 10; mobile phase, acetonitrile (AN) with a water content of 1.27, 2.27, 3.27 and 5.26% (v/v); one separation column; flow-rate, 0.25 ml/min; UV detection at 200 nm. 1 = Aniline; 2 = cyclohexanone oxime; 3 = adipimide; 4 = octahydrophenazine; 9 = ε-caprolactam.

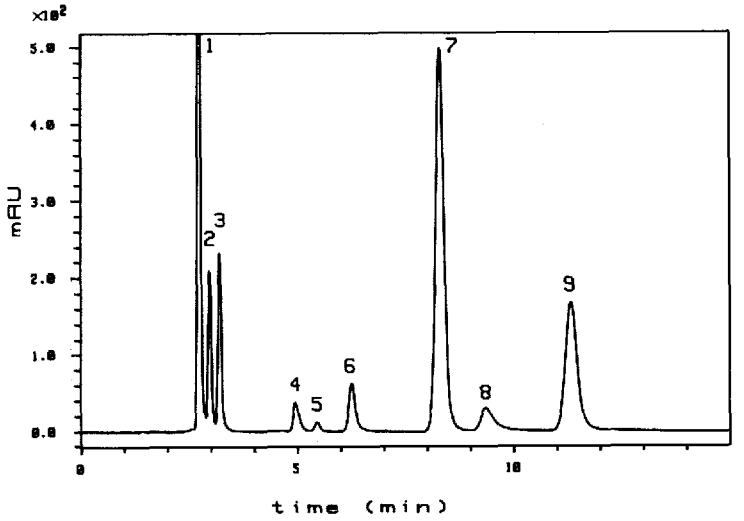


Fig. 2. Chromatogram of a test mixture of caprolactam impurities. Conditions: stationary phase, ES-Gel 10; mobile phase: acetonitrile–water (99:1, v/v); two separation columns in series; flow-rate, 0.42 ml/min; volume of test mixture, 0.5 μl; other conditions as under Experimental. Peaks: 1 = aniline (0.2 μg); 2 = cyclohexanone oxime (0.33 μg); 3 = adipimide (0.17 μg); 4 = octahydrophenazine (0.35 μg); 5 = *n*-valeramide (0.33 μg); 6 = ε-methyl-ε-caprolactam (0.13 μg); 7 = N-methyl-ε-caprolactam (1.25 μg); 8 = acetamide (1.5 μg); 9 = ε-caprolactam (0.6 μg).

TABLE I

RETENTION OF MODEL SUBSTANCES

Compound	t_R *(min)*[a]	*Compound*	t_R *(min)*[a]
Nitrobenzene	2.51	*n*-Capronamide	5.12
Dicyclohexanone	2.52	*n*-Valeramide	(5) 5.46
Tetrahydrobenzofurazan	2.55	N-*n*-Pentylacetamide	5.47
Dicyclohexanone oxime	2.59	N-Isobutylacetamide	5.69
Aniline	(1) 2.73	ε-Methyl-ε-caprolactam	(6) 6.38
Cyclohexanone	2.78	N-Methyl-ε-caprolactam	(7) 8.30
Cyclohexanone oxime	(2) 2.98	Acetamide	(8) 9.37
Adipimide	(3) 3.21	ε-Caprolactam	(9) 11.73
Octahydrophenazine	(4) 4.96		

[a] t_R = Overall retention time. The numbers in parentheses refer to the peaks on the chromatograms.

impurities. A deviation from the baseline at a retention time of 3.8 min, visible in some chromatograms, occurs when there are minor differences in the water content between the mobile phase and the sample solution.

Fig. 4 shows the chromatogram of pure caprolactam with a permanganate extinction number of 91. Only trace amounts of aniline and adipimide can be found. Adipimide had previously been found in all caprolactam samples examined.

Various spectra recorded with the diode-array detector are shown in Figs. 5a–c. Fig. 5a shows the reference spectrum of aniline, and Fig. 5d its spectrum recorded on the sample peak in the chromatogram in Fig. 3.

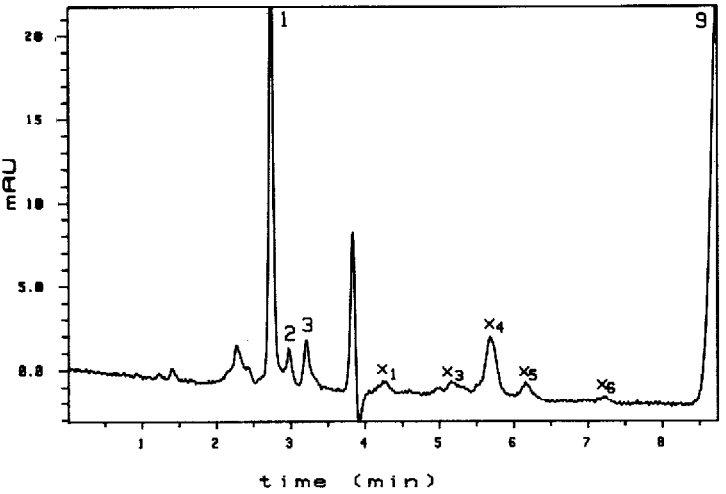


Fig. 3. Chromatogram of quality-reduced ε-caprolactam. Conditions: stationary phase, ES-Gel 10; mobile phase, acetonitrile–water (99:1, v/v); two separation columns in series: flow-rate, 0.42 ml/min; sample volume, 2 μl of solution from 10 g of sample in 25 ml of acetonitrile; other conditions as under Experimental. Peaks: 1 = aniline; 2 = cyclohexanone oxime; 3 = adipimide; 9 = ε-caprolactam; x_1–x_4, x_6 = unknowns; x_5 corresponds to C-methylcaprolactam.

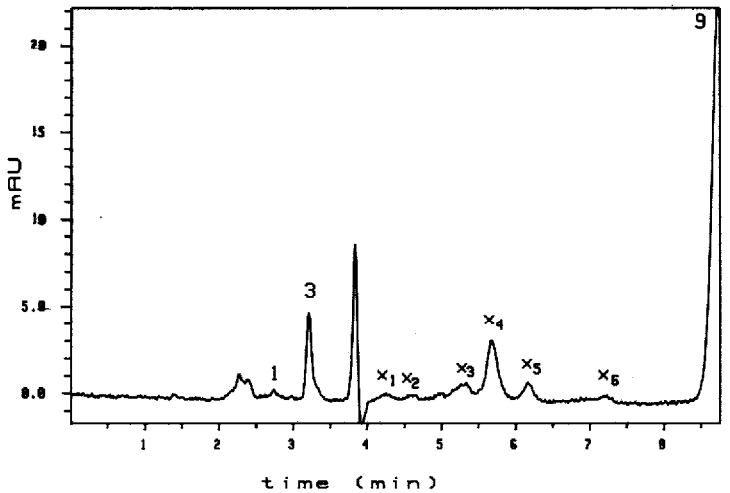


Fig. 4. Chromatogram of pure caprolactam. Conditions: stationary phase, ES-Gel 10; mobile phase, acetonitrile–water (99:1, v/v); two separation columns in series; flow-rate, 0.42 ml/min; sample volume, 2 μl of solution from 10 g of sample in 25 ml of acetonitrile; other conditions as under Experimental. Peaks: 1 = aniline; 3 = adipimide; 9 = ε-caprolactam; x_1–x_4, x_6 = unknowns; x_5 corresponds to C-methylcaprolactam.

Quantitative analysis

The external standard method was used to evaluate the chromatograms. In Table II, the slope m of the linear calibration function and the limit of determination c_m, measured as three times the noise level, are listed for some caprolactam impurities. The calibration slope represents the response factor, dependent on the substance used. If m is set to equal 1 for octahydrophenazine, the peak areas for equal amounts of

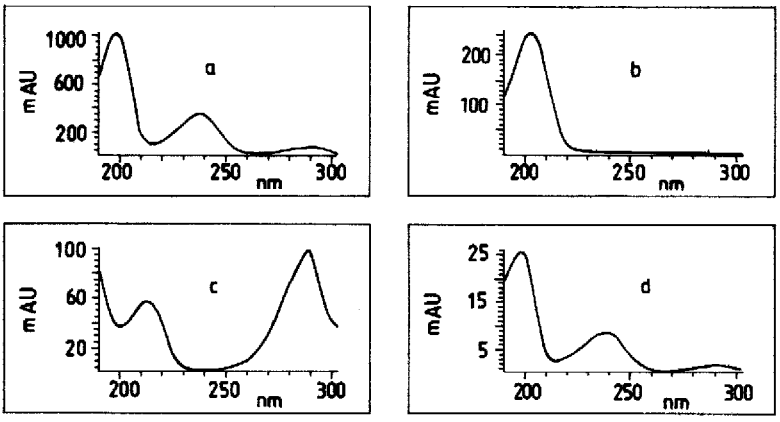


Fig. 5. UV spectra using the diode-array detector for peak identification. Conditions as under Experimental. (a) Peak 1 from Fig. 2 (aniline); (b) peak 3 from Fig. 2 (adipimide); (c) peak 4 from Fig. 2 (octahydrophenazine); (d) peak 1 from Fig. 3.

TABLE II

CONSTANTS OF THE CALIBRATION FUNCTION $y = mx$ OF INDIVIDUAL IMPURITIES AND THE MINIMUM AMOUNTS DETERMINED AFTER REGRESSION ANALYSIS[21]

Substance	*m (area/amount)*	*Limit of determination, c_m (ppm)*	*Correlation coefficient, r*
Aniline	21.4	0.1	0.998
Cyclohexanone oxime	3.4	0.5	0.999
Adipimide	6.6	0.5	0.999
Octahydrophenazine	2.0	1.0	0.999

octahydrophenazine, cyclohexanone oxime, adipimide and aniline are in the ratio 1:1.6:3.5:10.9. Some results for the determination of caprolactam impurities are given in Table III. As can be seen from Fig. 6, the content of aniline correlates with the permanganate extinction number according to ref. 3.

TABLE III

QUANTITATIVE EXAMINATION OF CAPROLACTAM SAMPLES FROM DIFFERENT MANUFACTURERS (I–IV)

Sample	*Aniline (ppm)*	*Cyclohexanone oxime (ppm)*	*Adipimide (ppm)*
Pure caprolactam I	0.1	<0.5	5.5
Pure caprolactam II	0.2	<0.5	3.4
Pure caprolactam III	<0.1	<0.5	3.2
Pure caprolactam IV	0.8	0.6	6.3
Depolymerization caprolactam	1.1	<0.5	71.7

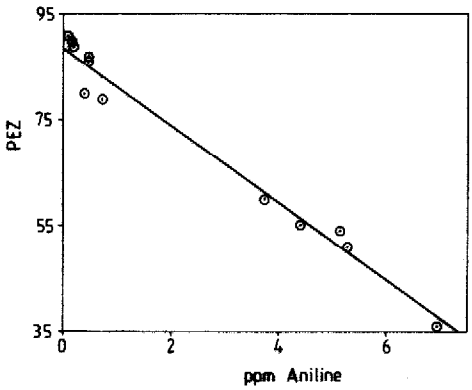
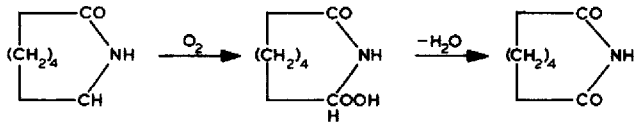


Fig. 6. Correlation between aniline content and permanganate extinction number (PEZ)[3] for caprolactam samples of different quality. Condition as under Experimental. Correlation coeffcient $r = -0.9891$; probability $P = 95.0\%$.

Thermo-oxidative deterioration

ε-Caprolactam is easily oxidized at high temperatures owing to its amide bond. As commercially it is stored, transported and further processed in a molten form, considerable attention must be paid to this point. Previous experiments showed that on exposure to oxygen, caprolactam (I) is converted primarily to the N-vicinal caprolactam hydroperoxide (II) and then to adipimide (III) (eqn. 1)[22–28]. Apart from adipimide, numerous other oxidation products, *e.g.*, valeramide, formyl-ε-caprolactam and cyclohexenecarboxylic lactam (1-[*H*]-7-oxo-4,5-dihydroazepine) can also be formed[27].



I II III

Gas chromatography has been applied to the characterization of thermo-oxidatively impaired ε-caprolactam. Under the preferred, alkaline conditions however, adipimide was not eluted and the degree of oxidation was concluded from the existence of an "oxidation peak"[6]. The fluorescence of the compounds with a ketoimide structure formed by thermo-oxidation of monomeric and polymeric ε-caprolactam has als been proposed as a measure of oxidative deterioration[29]. No significant differences could be detected in the samples of pure caprolactam using the latter method. The adipimide formed as the main product of thermo-oxidation of ε-caprolactam shows no fluorescence and so is not detected in this instance.

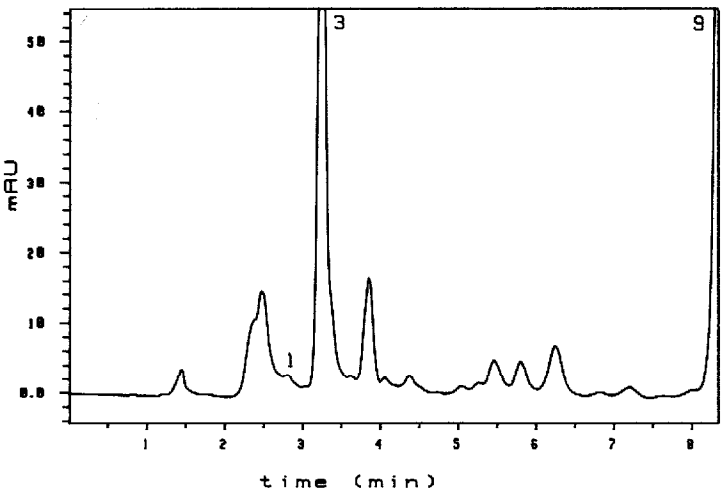


Fig. 7. Chromatogram of caprolactam from depolymerization. Conditions: stationary phase, ES-Gel 10; mobile phase, acetonitrile–water (99:1, v/v); one separation column; flow-rate, 0.21 ml/min; sample volume, 2 μl of solution of 10 g of sample in 25 ml of acetonitrile; other conditions as under Experimental. Peaks: 1 = aniline; 3 = adipimide; 9 = ε-caprolactam; other peaks unknowns. •

Using the HPLC method with silica and acetonitrile, a rapid, simple and sensitive means is available for measuring the oxidative deterioration of caprolactam. The slightest contamination can be accurately evaluated (compare Table II and Fig 4).

Fig 7 shows the chromatogram of a depolymerization caprolactam. The high adipimide content indicates a very strong oxidative action. The significant increase in the content of adipimide and of volatile bases on aeration of pure caprolactam can be seen in Table IV.

TABLE IV

RELATIONSHIP BETWEEN TIME OF AERATION, BASE NUMBER AND AMOUNT OF ADIPIMIDE DURING THERMO-OXIDATIVE DETERIORATION OF ε-CAPROLACTAM

Pure caprolactam was aerated at 100°C with 6.7 l/h of air.

Sample	*Aeration time (h)*	*Base number*[3] *(mmol/kg)*	*Adipimide (ppm)*
Pure caprolactam	0	0.17	8.5
Aerated samples	3	5.2	131.9
	3.5	8.6	214.1
	4	8.2	180.1
	4	8.6	224.6
	5	10.3	266.3

As further reaction products from the thermo-oxidation of ε-caprolactam, in addition to the key component adipimide, can be included in the determination of the volatile bases, *e.g.*, amines and ammonia of other origins, it was of interest to examine the connection between the adipimide content and the base number according to ref. 3. Fig. 8 shows that there is a linear correlation. The correlation was confirmed with samples of pure caprolactam of different origins. This demonstrates that the base number generally results from thermo-oxidative deterioration.

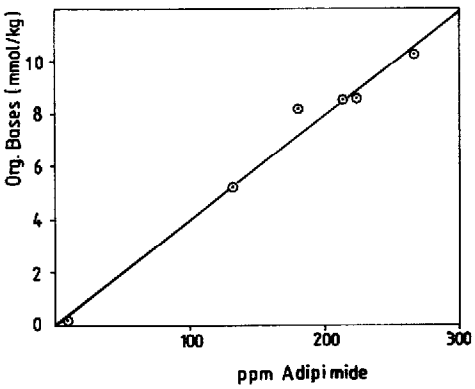


Fig. 8. Correlation between adipimide content and base number for samples of thermo-oxidative deteriorated ε-caprolactam. Conditions as in Table IV. Correlation coefficient $r = 0.9903$; probability $P = 95.0\%$.

The adipimide content determined by liquid chromatography can be defined as the thermo-oxidation value (TOV). The TOV lies in the range 1–100, corresponding to ppm or mg levels adipimide per kg of caprolactam.

CONCLUSIONS

This work has shown that HPLC on silica gel is well suited for the examination of caprolactam samples for technically relevant impurities. The conditions were found to be both simple and easily reproduced, and the previous history of the products can be derived from the chromatograms.

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