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Determination of Morpholine and N-Methylmorpholine Formed as Degradation Products in Cellulose Fiber Production by Capillary Isotachophoresis

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Capillary isotachophoresis with conductivity detection is applied for the determination of the degradation products morpholine and N-methylmorpholine in samples containing a large excess of N-methylmorpholine N-oxide, applied in spinning baths for the production of cellulose fibers. The analytes can be quantified at pH 7 of the leading electrolyte (0.01 mol/L K^+, morpholinepropanesulfonate as counterion) in concentrations above 30 ppm within 18 min with a relative standard deviation of about 3%. The decisive advantage of the method is the direct determination of the analytes without derivatization.

INTRODUCTION

For the production of cellulose fibers, spinning baths are applied, where the fibers are formed by coagulation or precipitation, respectively. In certain production units, these baths consist of highly concentrated aqueous solutions of *N*-methylmorpholine *N*-oxide (NMMO) with concentrations up to 20 wt %. During the long-term usage of these solutions, degradation products of NMMO are formed, which either can deteriorate the technical properties of the spinning baths with respect to the quality of the fibers produced or affect the purity of NMMO, being recovered from the precipitation solutions on a preparative scale.

The main degradation products formed from NMMO during fiber production are *N*-methylmorpholine (NMM) and morpholine (M). As a consequence, their content in the spinning baths must be monitored on the one hand and must be determined during the recovery process of NMMO on the other hand.

The determination of NMM and M in the presence of a large excess of NMMO is not described yet in the literature, although for similar concentrations of these solutes, their separation is described with high-performance liquid chromatography (HPLC) (*1*). However, this method requires a complicated procedure including the application of two HPLC systems with mobile-phase gradients, one even nonlinear. Therefore, this method is of limited use for routine analysis, especially for large concentration differences of the analytes.

The acidimetric titration of the amines in the presence of the amine *N*-oxide, also described (*2*), leads to a sum parameter including all these components, because they cause the same end points. In order to determine the content of the amines, a second titration must be carried out after the derivatization of the amines, and their concentration is determined from the difference of the results obtained. This procedure is not only time consuming but also often leads to large systematic errors, especially when the *N*-oxide is present in a large excess. Further, the most important disadvantage of this method is that only the sum of the concentrations of NMM and M, but not their single contents, is obtained.

Table I. Electrolyte Systems Applied for the Isotachophoretic Determination of Morpholine and *N*-Methylmorpholine[a]

	cation	counterion	concn, mol/L	pH
leading electrolyte	K^+	MOPS[b]	0.01	7.0
terminating electrolyte	TBA^+[c]	ClO_4^-	0.01	7

[a] No additive was used. [b] Morpholinepropanesulfonate. [c] Tetrabutylammonium.

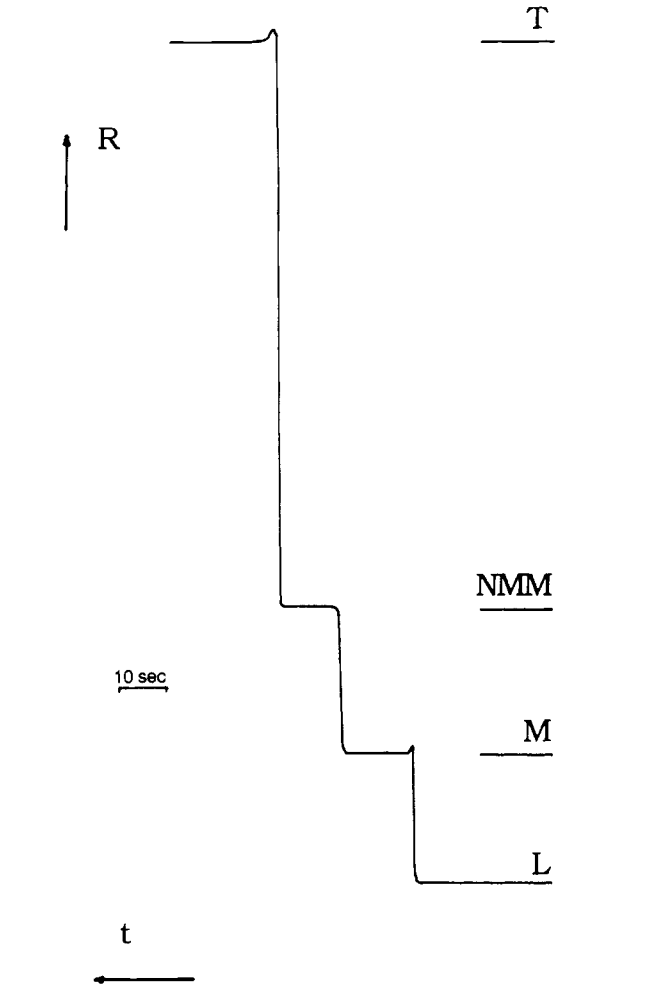

Figure 1. Isotachopherogram of a model mixture of morpholine (M) and *N*-methylmorpholine (NMM). Injected amounts: about 400 ng of each. Key: (L) leading ion; (T) terminating ion; (R) electric resistance; (t) time.

The determination of the analytes by gas chromatography is limited by the fact that the main sample component,

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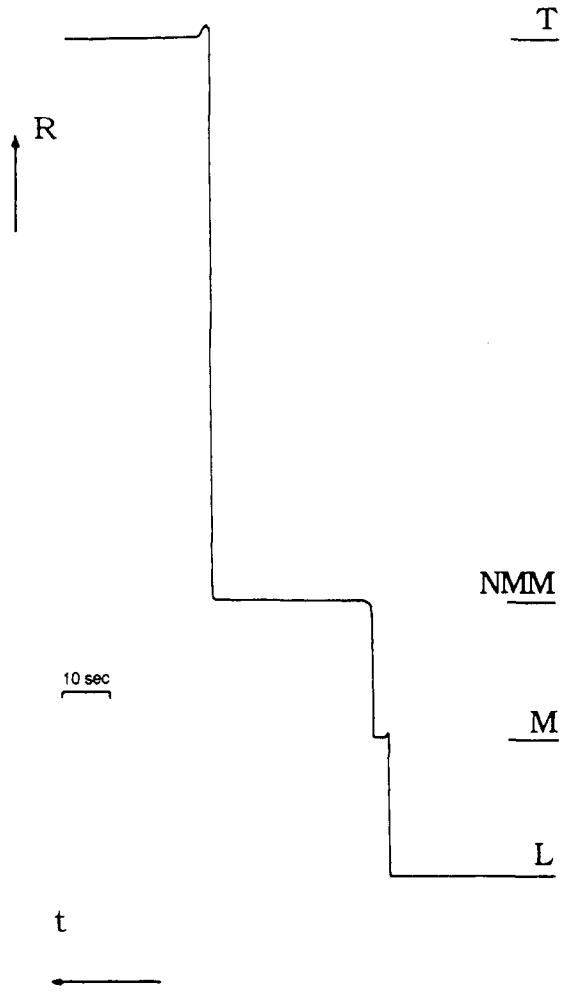

Figure 2. Isotachopherogram of a 20% aqueous solution of commercial *N*-methylmorpholine *N*-oxide as applied as a spinning bath for the production of cellulose fibers. Symbols are as in Figure 1.

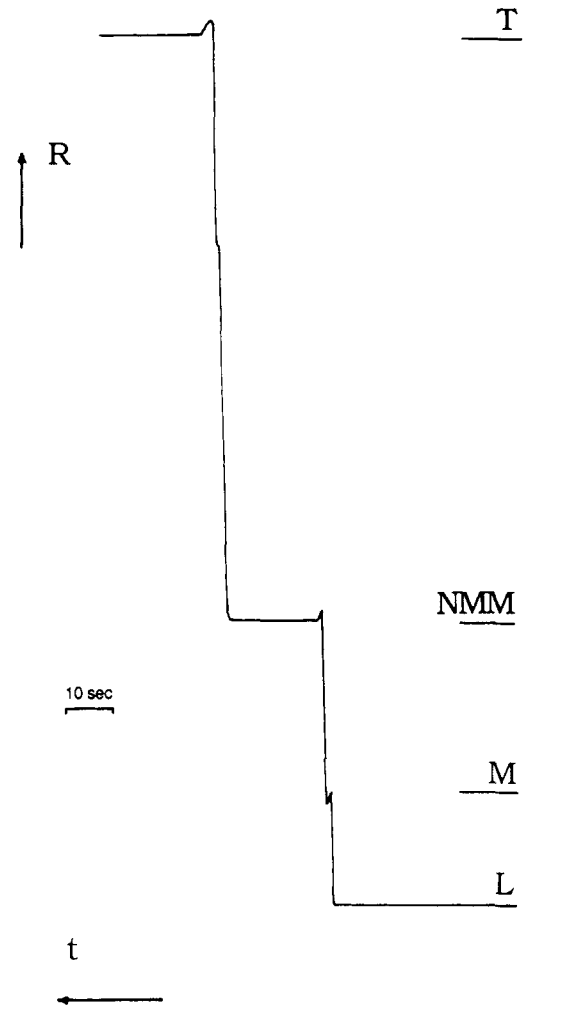

Figure 3. Isotachopherogram of a spinning bath, consisting of an about 20% aqueous solution of NMMO with diethylenetriamine as stabilizer. Symbols are as in Figure 1.

NMMO, is thermally unstable and undergoes degradation during gas chromatographic determination of the analytes (2), forming NMM and M as artifacts.

Separation based on isotachophoresis (ITP) coupled with conductimetric detection, seems to offer an ideal combination to solve these types of analytical problems, because the identical analyte properties are used for the separation and for the detection: the effective ionic mobility. It is the same physicochemical property that is also applied for the separation in free capillary zone electrophoresis (CZE). In fact, both techniques differ only in the arrangement of the buffer electrolytes in the separation system (cf., e.g., ref 3). In CZE the entire capillary is filled with a single buffer, which has a relatively high concentration, compared to the analytes. In contrast, in ITP the separation capillary is filled with a discontinuous buffer: one, the leading electrolyte, has the ions of the highest mobility (only those ions are considered which have the same sign of electrical charge as the analyte ions); the other, the terminating electrolyte, has the ions with the lowest mobility of all ions of interest. The analytes, with mobilities between those of the leading and terminating ions, are injected in between the two system electrolytes. Due to this arrangement the sample ions themselves consequently must transport the electric current in their respective zones, when an electric field is applied, because the current is not transported almost exclusively by a carrier electrolyte as in CZE. After separation, the analyte zones are migrating directly one after the other with equal migration velocity. They are not separated by zones formed by the carrier electrolyte.

As a further consequence of the spacial arrangement of the electrolytes in ITP, the concentrations of the ions are adjusted to distinct values, depending on the concentration of the leading electrolyte, according to the so-called "regulating function", which was introduced by Kohlrausch about 100 years ago. Thus ITP can act as an enrichment method, also in contrast to normal CZE, where the analytes are diluted by the buffer solution during migration.

Within the sample zone the analyte concentration is constant in ITP, thus giving a rectangular concentration distribution of the analyte, in contrast to the Gaussian distribution obtained in CZE. If the amount of analyte increases, the zone length increases too. Therefore this length is the parameter for quantitation.

As the analytes must have different ionic mobilities to enable separation, the resolved zones must have different electric resistance: therefore a conductimetric detector allows the identification of the analytes based on the corresponding step heights in the isotachopherogram. It follows that, advantageously, the conductimetric detector signal is caused only from the analyte (and the counterion) and not from the relatively concentrated carrier electrolyte too, which is the case in CZE.

Both analytes of interest for the problem under consideration, NMM as M, can be converted into ions; therefore, in this paper, the conditions for the isotachophoretic separation of the analytes in an excess of NMMO are discussed and an appropriate method for their quantitation is presented.

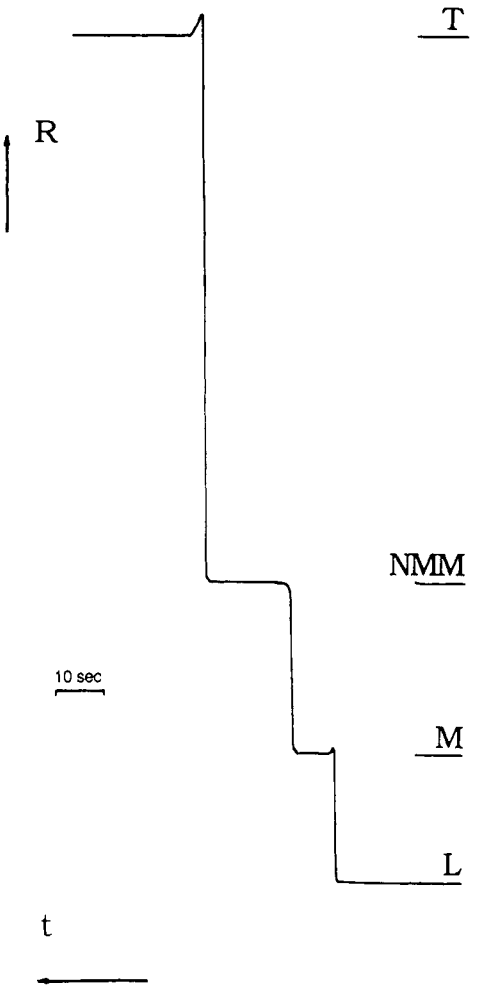

Figure 4. Isotachopherogram of the aqueous distillate obtained by the recovery of NMMO from a spinning bath. Symbols are as in Figure 1.

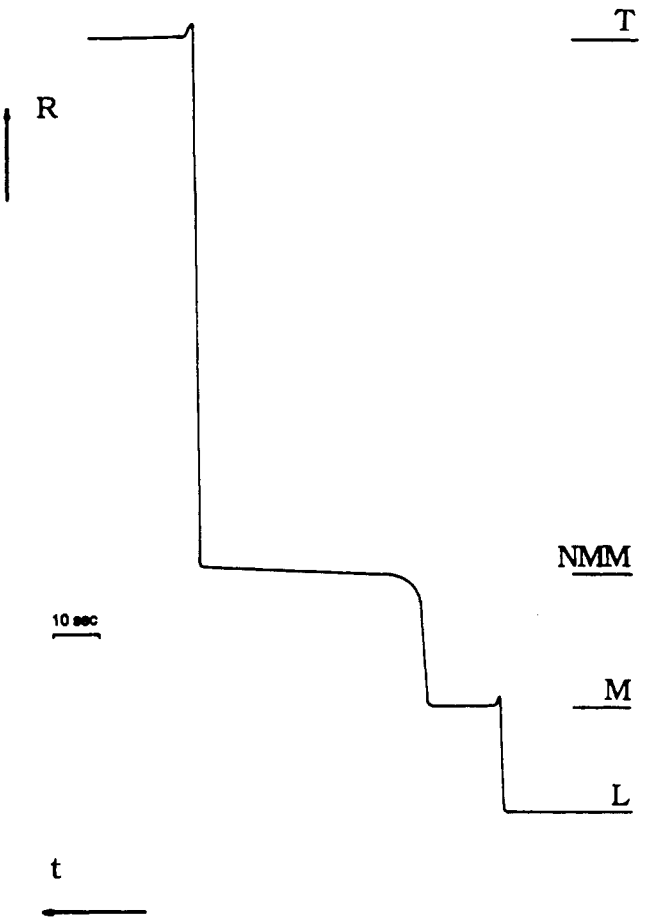

Figure 5. Isotachopherogram of a 20% aqueous solution of NMMO after treatment at elevated temperature. Symbols are as in Figure 1.

EXPERIMENTAL SECTION

Chemicals. Chemicals used for the preparation of the buffers were of reagent grade (E. Merck, Darmstadt, GFR). The reference substances were "for synthesis" (E. Merck). Water used as the solvent was distilled twice from a quartz apparatus.

Apparatus. The isotachophoretic measurements were carried out by a homemade instrument according to Everaerts (*3*), which consisted of a separation capillary made from polytetrafluoroethane (25-cm lengths, 0.3 mm i.d.), equipped with an electrical conductivity detector directly mounted into the capillary. A constant current of 50 μA was applied by using a high-voltage power supply unit (Model Alpha 2807, Brandenburg, Thornton Heath, U.K.). The detector signal was recorded with a strip chart recorder (Kompensograph III, Siemens, Karlsruhe, GFR) at 6 cm/min. The measurements of the zone heights and lengths were carried out manually.

Procedure. No special sample pretreatment was carried out. The samples were diluted with water to an appropriate analyte concentration, and microliter volumes of the sample solutions were directly injected into the isotachophoresis instrument with a precision syringe.

RESULTS AND DISCUSSION

Adjustment of the Separation Conditions. The requirements on the electrolyte systems applied for the isotachophoretic separation and determinations of morpholine and *N*-methylmorpholine can be derived from the acid/base properties of the sample components, whereby the properties of the analytes as well as those of the matrix constituents must be taken into account. These substances are either neutral under the given conditions (e.g. matrix components like cellulose or propylgalleat added as stabilizer) or acidic (like carbonic acid or hydroxycarboxylic acids, formed by the degradation of cellulose), or they behave as bases like the analytes, forming cations in their protonated form (besides diethylenetriamine (DTA), used as a stabilizer, NMMO, which is the major component). Because in isotachophoresis, where electroosmosis is usually suppressed, sample components with the same sign of the charge (only cations and anions, respectively, but no neutrals) are migrating in the separation system toward the detector, anions or neutrals will not interfere with the determination of the analytes under appropriate separation conditions. The adjustment of the pH of the buffering electrolyte systems has to focus therefore on the electrophoretic behavior of NMMO, NMM, M and DTA.

In a first step, the electrolyte system is therefore chosen such that interference by the major component, NMMO, is eliminated by selecting a pH where NMMO is not protonated (or charged to such a minor extent, that its effective mobility is sufficiently low) and is therefore not migrating electrophoretically within the isotachophoretic zones. Obviously, the pH has to be chosen such that the analytes can be separated. On the basis of the pK values of the components of interest (7.38 for NMM, 8.50 for M, <5 for NMMO, and >9 for DTA (*4*)), buffering systems with pH values between 6.5 and 7.5 seemed to be most favorable. Through the application of such systems, it was found experimentally that the leading electrolyte with pH of 7.0, given in Table I, had the best properties for the separation of the analytes.

The result of this selection, based on the different degree of protonation, is presented in Figure 1, showing the separation of morpholine and *N*-methylmorpholine from pure aqueous standard solutions. It can be seen further from Figure 2,

showing the isotachopherogram of a concentrated solution of commercial NMMO (20%, w/w, in distilled water) and DTA (2%, w/w), that the main component in this solution, NMMO, does not appear in the isotachopherogram, because its effective mobility is too low for isotachophoretic migration, lower than the mobility of the terminating ion. Furthermore, DTA does not appear in the isotachopherogram, because its high degree of protonation leads to an effective mobility that is higher than that of the leading ion. From these reasons, a buffering leading electrolyte system with pH 7, consisting of the leading and terminating ions described, is used for the quantitation of NMM and M in all samples.

Determination of Morpholine and *N*-Methylmorpholine in Industrial Samples. In Figures 3–5 isotachopherograms obtained from typical samples are shown. It can be seen, that in all samples NMM and M can clearly be recognized without interferences from other components. Thus, the quantitation of the analytes can be carried out by the use of the calibration lines, given by the following equations, where the zone lengths, y (in millimeters), are related to the amounts of analyte injected, x (in nanograms): NMM $y = 0.0320x$; M $y = 0.0423x$. The intercepts of both lines do not differ from zero on the 5% significance level. The linear correlation coefficients were 0.9994 and 0.9988, respectively, for the measured range of about 800 ng.

The lower detection limit for the determination of both analytes was about 30 ng injected, corresponding to about 30 ppm for the technical solutions. The precision of the measurements, expressed by the relative standard deviation, was 3.3% (five measurements). It was derived from the manual determination of a zone with a recorded length of about 1 cm. The time of an isotachophoretic run was about 18 min.

The results of the quantitation of the analytes in commercial NMMO and in the typical samples shown in Figures 3–5 are given in Table II. Because all sample components are water soluble and no complexing agents are present, a total yield of the analytes of about 100% can be expected. Within the measuring error, this result was in fact found by standard addition.

Table II. Concentrations of *N*-Methylmorpholine (NMM) and Morpholine (M) in Different Samples

sample	concn, ppm NMM	concn, ppm M
commercial *N*-methylmorpholine *N*-oxide	640	30
spinning bath (DTA containing)	420	<30
NMMO solution after heat treatment	5500	480
distillate from NMMO recovery	4150	730

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