Determination of the amount of wash amines and ammonium ion in desulfurization products of process gases and results of related studies ☆

Marian Kamiński[a,b,*], Daniel Jastrzębski[b,c], Andrzej Przyjazny[d], Rafał Kartanowicz[b]

[a]*Quality Control Department, Refinery of Gdańsk, 80-718 Gdańsk, Poland*
[b]*Analytical Chemistry Department, Chemical Faculty, Technical University of Gdańsk, 80-952 Gdańsk, Poland*
[c]*Quality Control Department, Pharmaceutical Works "POLPHARMA", 83-200 Starogard Gdański, Poland*
[d]*Kettering University, 1700 West Third Avenue, Flint, MI 48504, USA*

Abstract

This paper describes a method for the determination of the so-called wash amines and their degradation products, including ammonium ions, in process liquids and wastewater generated during the desulfurization of hydrogen sulfide gas in the process of crude oil refining and also reports the results of related studies. Ion-exchange liquid chromatography employing an inexpensive cation-exchange HPLC column and refractometric detection was used. The results obtained were compared with those obtained by potentiometric titration. Analytical characteristics and a description of the developed procedure are provided. Examples of the results of routine determinations of amines, their degradation products and ammonium ions in process liquids and wastewater are given.   © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Desulfurization products; Crude oil refining; Wash amines; Alkanolamines; Ammonium ion

1. Introduction

Modern processes of crude oil refining, utilizing catalytic hydrorefining, reforming, and hydrocracking, result in the formation of large volumes of gases containing hydrogen sulfide. In order to remove hydrogen sulfide from the post-refining gases, a so-called amine wash is employed. This process makes use of the absorption affinity of hydrogen sulfide to amines such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), etc., followed by desorption of the hydrogen sulfide from the absorption liquid by steam under boiling conditions.

An amine solution can undergo thermal and chemical degradation in desulfurization processes, particularly when the hot aqueous amine solution is in contact with oxygen-containing compounds such as sulfur dioxide, carbon dioxide, carbon monoxide or gaseous oxygen. This results in the formation of secondary compounds, both acidic and basic [1,2]. Ammonia and ammonium cations are also formed, which is especially evident in the reflux recirculated to the process or removed as wastewater. A consider-

*Corresponding author. Quality Control Department, Refinery of Gdańsk, 80-718 Gdańsk, Poland.
E-mail address: marian.kaminski@rgsa.pl (M. Kamiński).

able degree of degradation of amines results in a substantial decrease in the effectiveness of hydrogen sulfide removal through desulfurization processes and accelerated corrosion of plant installations [1–3]. As a result of technological malfunctions, there is the possibility of transporting to the wastewater treatment plant not only lyes, rinse water and column refluxes, but also process amines and their degradation products, including ammonium ions. Hence, it is important to determine the concentration and the degree of degradation of the amines used in the desulfurization processes as well as their acidic and basic degradation products in water, lyes and process wastewater. The total content of acidic products in wash amines solutions is determined by binding all cations present in a sample using a cation-exchange column packed with a strong cation-exchanger in the hydrogen form. The acids formed after the exchange of amines and other cations originally present in the sample into protons are then titrated with a standard base solution [4]. Anion-exchange HPLC with gradient elution is used to determine the concentration of individual anions [5].

Modern cation-exchange liquid chromatography with ion suppression and conductometric detection (ion chromatography) can be used for the determination of the concentrations of amines (MEA, MDEA, DEA, etc.) in process liquids resulting from desulfurization of gases generated in the refining and petrochemical industries [5]. However, acid–base titration in the presence of an indicator or potentiometric titration using a glass electrode are two common methods employed in the industry [6,7].

Our experience indicates that the results of determinations of amines by acid–base titration may be erroneous when the degree of amine degradation is considerable, or when the examined sample contains a number of different amines, and/or when the examined sample in addition to the amine being determined also contains ammonium ions at concentrations above 0.1%. Acid–base titrations in the presence of a dye indicator as well as potentiometric titrations are not sufficiently selective to enable the simultaneous determination of an amine and ammonium ion.

Thus, the ability to correctly determine the concentration of a wash amine and its basic degradation products, including ammonium ions, in process liquids and wastewater resulting from the process of amine desulfurization is important for the evaluation of desulfurization process control and for the diagnosis of sources of nitrogen pollution of wastewater.

There are papers describing the use of HPLC for the separation of amines in the reversed-phase (RP) mode without derivatization [8] but with poor resolution, or with precolumn derivatization and separation of nonionic derivatives [9], or the use of ion chromatography with conductometric or potentiometric detection [10–13]. A particularly thorough analysis of the problem of separating this type of substance on an ion-exchange column was provided by Vialle et al. [12]. However, the authors did not apply the results obtained to the practical determination of amines in process liquids, and the simultaneous separation and quantitation of ammonium ions was not considered.

A recent paper by Kadnar [13] describes an ion chromatographic method for the determination of selected alkanolamines, corrosion inhibitors, alkali and alkaline earth metals in water and process liquids of a crude oil refinery. The method makes use of CS10 and CS12A cation-exchange columns (Dionex, USA) based on sulfonated styrene–divinylbenzene copolymers, ion suppression and pulsed conductometric detection along with gradient elution. MDEA and other alkanolamines as well as corrosion inhibitors can be determined in the presence of alkali metal ions; however, alkaline earth metal ions interfere with the determination because their peaks overlap those of ethanolamines. Other disadvantages include the substantial cost of the columns and the need for up to a 10 000-fold dilution of a sample of 40% process amine, which increases the error of determination. In addition, our experience indicates that the use of an ion suppressor for samples of process liquids and wastewater from the desulfurization process results in a surprisingly rapid deterioration of the suppressor membrane, leading to frequent replacement, which is both expensive and time-consuming.

This paper describes a simple method for the determination of wash amines and their degradation products, including ammonium ions, in process liquids and wastewater associated with the amine desulfurization process, using cation-exchange liquid chromatography and refractive index detection.

2. Experimental

2.1. Materials

The analytes studied included amines used in gas desulfurization processes: monoethanolamine (MEA; Merck, Germany, AR grade), diethanolamine (DEA; Merck, AR grade) and methyldiethanolamine (MDEA; DOW Chemical, USA, technical, 99.6% pure), butyldiethanolamine (BDEA; Sigma–Aldrich, USA, pure) and NH_4Cl, $NaCl$, KCl, $CaCl_2$, $MgCl_2$, and $FeCl_2$ (POCh, Gliwice, Poland).

The mobile phase for HPLC was prepared using potassium or sodium dihydrogen phosphate (KH_2PO_4; Merck, AR grade) (NaH_2PO_4), orthophosphoric acid (H_3PO_4; 85% w/w; Merck, AR grade), deionized water, acetonitrile (Merck, gradient HPLC grade) and potassium nitrate (KNO_3; Merck, AR grade).

2.2. Apparatus

A Merck–Hitachi Lichrograph HPLC equipped with a L-6200 gradient pump, a R-7000 refractometric detector, a T-6300 column thermostat and a Rheodyne RH-7124 injector with a sampling loop volume of 20 μL were used for chromatographic investigations. A 250×4.6 mm Macherey–Nagel HPLC column packed with Nucleosil SA 5 μm was employed. In some experiments, a Merck–Hitachi L-4500 diode-array detector (DAD) was also used.

A Metrohm Titrino potentiometer equipped with a glass indicator electrode and a calomel reference electrode was used for potentiometric titrations.

2.3. Procedure

The use of a refractometric detector precludes gradient elution. An isocratic ion-exchange HPLC system using different concentrations of mobile phase components was employed with the column operating at 30 °C. The mobile phase flow-rate was either 1 or 2 ml/min. Solutions of inorganic salts and amines were introduced onto the column at concentrations ranging from 0.01 to 40% by weight. An external standard method with the assumption of linearity of calibration curves was used for quantitative analysis. Calibration was carried out for amine and inorganic ion concentrations ranging from 0.01 to 1.5% by weight.

A potentiometric titration procedure CTM5-9 for the determination of free amines and so-called bound amines, developed by Chevron Research and Technology (USA) [7], was also employed. In addition, the standard Nessler method and the indophenol method for determining ammonium ions were used.

3. Results and discussion

3.1. Eluent selection

A major objective of this study was to select an optimum composition of the mobile phase to separate amines, their important basic degradation products and ammonium ion (ammonia) as well as measuring the retention times of sodium, potassium, magnesium, calcium and iron (II) ions, which can be present in process wastewater samples and possibly interfere with the determination of amines and/or ammonium ion. The selection of the mobile phase was performed by a trial-and-error method using various ratios of KNO_3, NaH_2PO_4, KH_2PO_4, water, 85% H_3PO_4 and acetonitrile. The concentration of salts in the mobile phase was varied between 0.03 and 0.2 M, the acetonitrile content was varied from 0 to 33% (v/v), and the concentration of 85% H_3PO_4 was varied from 1.5 to 2.5 mL/L, which resulted in a pH change from 3.8 to 1.8, respectively.

A 0.088 M aqueous solution of KH_2PO_4 acidified with 85% H_3PO_4 solution to pH 2.6 was found to be optimum. The addition of acetonitrile to the eluent reduces the retention of alkanolamines. The shortening of the elution time resulting from the increased acetonitrile content of the eluent is greater for the more hydrophobic alkanolamines, for example BDEA. Consequently, purely aqueous mobile phases were used in further experiments.

During these studies, use was made of the principle well known in ion-exchange chromatography that the retention times of ions decrease with an increase in ionic strength of the mobile phase at a specified pH. However, we also made use of the fact that, in a Nucleosil SA and related columns, lowering the ionic strength of the mobile phase increases the retention time of inorganic cations less than that of

alkanolamines. Presumably, this can be explained by hydrophobic interactions between alkanolamines and arylsulfonic groups bonded to silica gel in addition to the ion-exchange phenomenon. Fig. 1 shows chromatograms obtained with the optimum mobile phase for ammonium, MEA, DEA and MDEA (chromatogram A), a 20-fold diluted process water solution of MDEA (chromatogram B) and a solution of bicine, sodium, magnesium and calcium ions (chromatogram C).

The order of elution when using the optimum mobile phase composition was: anions, water, very weak organic bases (e.g., bicine, oxazolidone), Na^+ (negative peak when the mobile phase contains potassium ions or very low sensitivity when the mobile phase contains sodium ions), NH_4^+, MEA and K^+ (when the mobile phase contains sodium ions or low sensitivity for potassium ions when the mobile phase contains potassium ions), DEA, MDEA, Fe^{2+} and Mg^{2+} (not separated), Ca^{2+}, and BDEA. It should be emphasized that, under the developed optimum conditions, not all the above ions can be determined due to incomplete separation of MEA and K^+, and Fe^{2+} and Mg^{2+}. On the other hand, MDEA, Mg^{2+} and Ca^{2+} can be determined simultaneously, which would be impossible if the mobile phase contained a concentration of potassium salt ≥ 0.1 *M*.

Other salts (NaH_2PO_4 and KNO_3) investigated as possible additives to the mobile phase were judged unsuitable and were not used in the optimized procedure for the following reasons.

(i) KNO_3 has a too high refractive index (and UV absorbance), which lowers the sensitivity of the method and makes it impossible to use UV detection to determine aromatic heterocyclic compounds and other UV-absorbing basic substances, sometimes present in waste water samples from the hydrorefining of crude oil fractions (e.g. in water condensates from base oil refining).

(ii) NaH_2PO_4 has a lower refractive index than KH_2PO_4. It should improve the sensitivity of the determination of ammonium and ethanolamines. However, the use of NaH_2PO_4 results in slightly
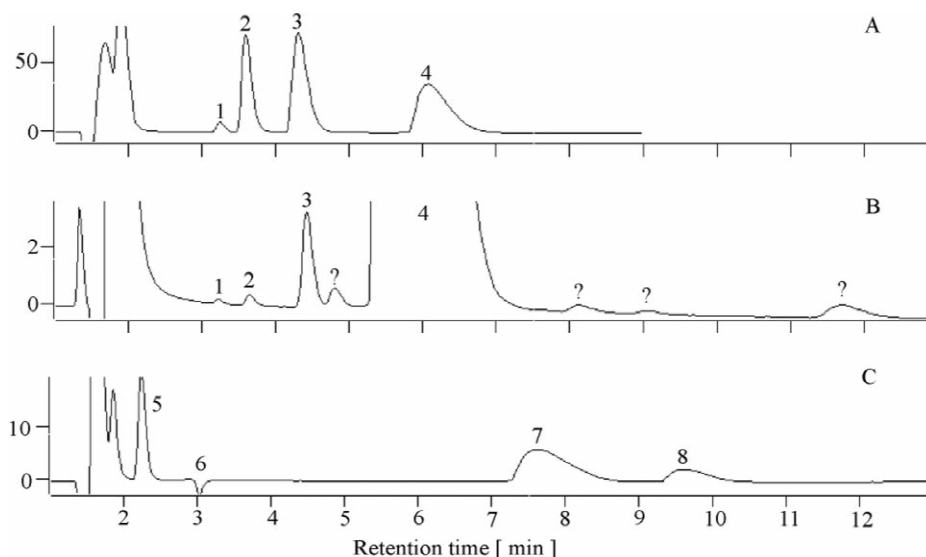

Fig. 1. Chromatogram A: water-diluted MDEA (peak 4) process sample spiked with ammonium (peak 1), MEA (peak 2) and DEA (peak 3). Chromatogram B: 40-fold diluted process sample of the ''lean'' amine MDEA from the outlet of the desulfurization column (point 650 P4) shown at a high sensitivity of the RI detector (peak 4: MDEA, $t_R = 5.76$ min, concentration 0.983%); for the other peaks, see the description for chromatogram A (''?'' marks the peaks of unknown substances). Chromatogram C: bicine (peak 5), sodium (peak 6), magnesium (peak 7) and calcium ion (peak 8). Conditions: column, Nucleosil SA 5 μm 250×4.6 mm; eluent, 0.088 mol/L KH_2PO_4 acidified with 85% H_3PO_4 to pH 2.6; temperature, 30 °C; mobile phase flow-rate, 2 ml/min; detector, RI.

more broadened chromatographic peaks and the gain in sensitivity becomes negligible. Additionally, the determination of sodium (like ammonium) is often important in refinery waters and wastewater samples. The determination of potassium ion is, in most cases, insignificant in technological refinery processes, since the use of sodium or ammonium ions in the mobile phase should not occur. It precludes, as a consequence, the identification and determination of low concentrations of sodium or ammonium ions.

3.2. Characteristics of the method for the determination of NH_4^+, MEA, DEA and MDEA in process water

A pure or two- to 40-fold water diluted sample (the concentration of the determined compounds should not be >1.5 wt%) was filtered through a 0.45 μm filter. A 20 μL sample volume was injected using a manual injector. A small-volume sample loop, for instance 1 μL, makes the injection of a pure sample possible. This will enable the on-line use of the described method. The total determination time is 10 min.

The method allows direct quantitative determination of all the above amines and ammonium ions

as well as other basic amine degradation products (such as bicine or oxazolidone). It should be pointed out that DEA is the main contaminant of technical MDEA solution and a major basic degradation product of MDEA.

Satisfactory linearity in the range from 0.01 to 1.5 wt% (correlation coefficients >0.998) for all the investigated alkanolamines, ammonium ion, alkali metal and alkaline earth metal ions and Fe^{2+} was obtained. An increase in concentration above 2% by weight results in significantly reduced retention times and peak broadening due to column overload. Examples of RI chromatograms obtained for calibration are shown in Fig. 2. For a 20 μL sample, the lower limit of detection (LLD) for NH_4^+, MEA, DEA, and MDEA is 0.012, 0.0025, 0.0033, and 0.004%, respectively.

The described method also allows the determination of metal ions, including Na^+ (negative peak), Mg^{2+}, Fe^{2+}, and Ca^{2+}; however, the presence of Mg^{2+} at levels $>0.01\%$ causes interference with Fe^{2+} (see Fig. 1).

In the analysis of wastewater samples, the additional use of UV detection at approximately 270 nm or UV-DAD in series with the RI detector is possible. In this case, it is possible to ensure that aromatic amines and other basic UV-absorbing substances do
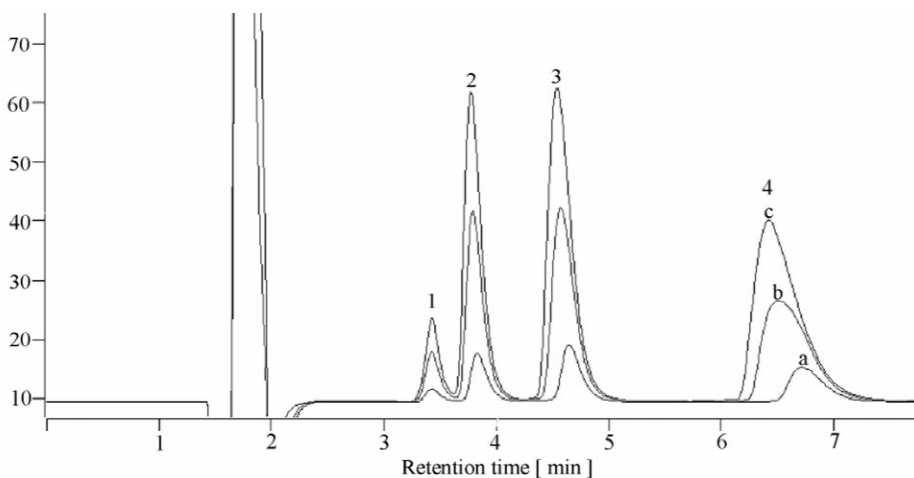

Fig. 2. Examples of chromatograms of ammonium ion (NH_4^+; peak 1, $t_R = 3.43$ min), monoethanolamine (MEA; peak 2, $t_R = 3.80$ min), diethanolamine (DEA; peak 3, $t_R = 4.60$ min) and methyldiethanolamine (MDEA; peak 4, $t_R = 6.60$ min). Concentrations approximately 0.5% (c), 0.25% (b), and 0.067% (a). Conditions as in Fig. 1.

not interfere with the determination of ammonium and alkanolamine (see Fig. 4).

3.3. Application of the procedure to process liquid and wastewater analysis

The procedure described above has found application in the determination of wash amines MDEA and MEA as well as ammonium ions and other basic degradation products in lyes and process wastewater of the Gdańsk Refinery. Good agreement between the results determined and the true concentrations was obtained both for samples with high amine concentrations and low ammonium ion concentration (solution of a so-called ''lean'' process amine from the absorption column inlet of the amine wash installation; point 650 P4, Fig. 1B) and for samples with a high ammonium ion content and a low MDEA concentration (reflux of a desorption column; point 650 C5, Fig. 3).

The method was also used to determine amines and ammonium ions in the wastewater entering a water treatment plant, in holding tanks containing wastewater from a desulfurization installation, in so-called stripper of acid water, and in the conden-

sates from the hydrorefining of base oils or from beneath the flare. Good agreement was obtained between the results obtained by the method under discussion and the indophenol method after the samples were appropriately diluted. It was observed that the Nessler method, when used for these liquids, yields high results even for appropriately diluted samples and, therefore, it cannot be applied to the determination of ammonium ions in wastewaters from crude oil refining.

When determining the concentration of ammonium ion and/or ethanolamines in the process wastewater of a crude oil refinery it is appropriate to connect a UV (270 nm) or a diode-array detector (DAD) in series before the refractive index detector. This allows the identification of the presence of aromatic amines or heterocyclic nitrogen compounds in the investigated samples and, if the need arises, their determination. It should be pointed out that, in some types of wastewater or process liquids (e.g., in the condensate beneath the flare, in the rinse water for gases from vacuum distillation or from hydrorefining of base oils), the concentration of aromatic organic bases can be substantial and even in chromatograms obtained with RI detection their peaks
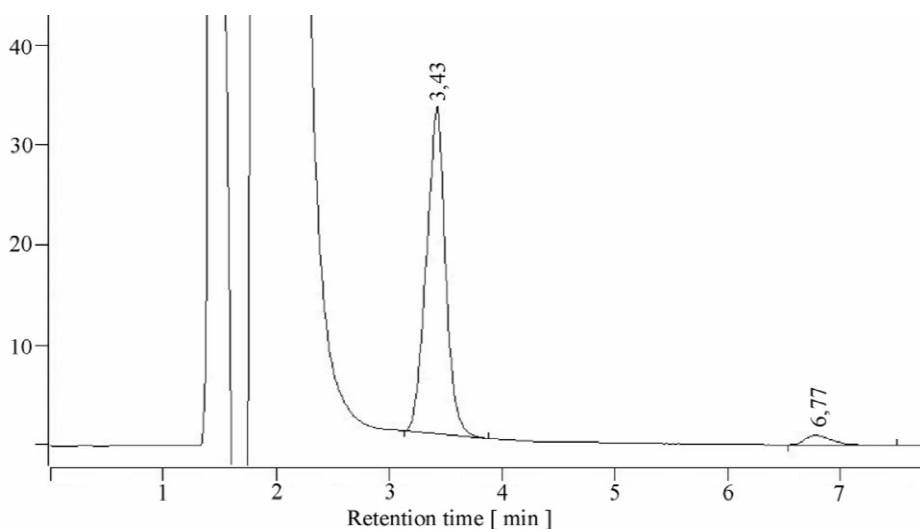

Fig. 3. Chromatogram of a 10-fold diluted sample of reflux from the desorption column (point 650 C5); ammonium ion (t_R = 3.43 min, concentration ca. 0.25% after dilution), MDEA (t_R = 6.77 min, concentration ca. 0.005% after dilution). Conditions as in Fig. 1.

may overlap with the peaks corresponding to ammonium ion and/or ethanolamines, resulting in errors of determination. Fig. 4 shows examples of chromatograms obtained using DAD and RI detectors for samples of rinse water used for gases generated in the hydrorefining of base oils. The chromatograms reveal the presence of ammonium ion, the concentration of which can be determined with a certain error due to the overlap of the peak with that of another base, as well as the presence of aromatic organic bases. Over the 1-year period when the method described in this paper was employed in

the Gdańsk Refinery to determine ammonium and ethanolamines using 0.1 M KH_2PO_4 as the mobile phase, such an overlap occurred several times. For this reason, the concentration of KH_2PO_4 was reduced to 0.088 M, which somewhat increased the analysis time, but provided a better separation from heterocyclic compounds.

3.4. Potentiometric determination of amines and ammonium ion
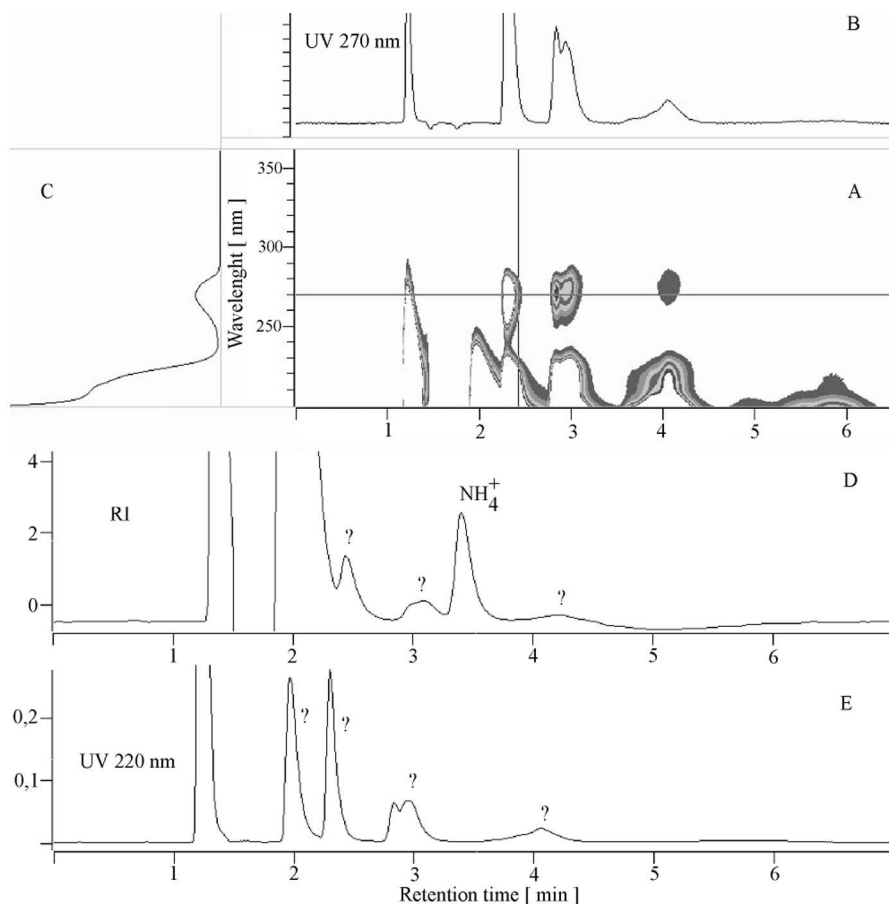
The potentiometric method (CTM 5-9) for the

Fig. 4. Chromatograms of a sample of the wastewater and steam condensate flowing from a catalytic reactor for the hydrorefining of base oils, obtained using UV-DAD (chromatograms A, B, and E, and UV spectrum C) and RI (chromatogram D) detectors connected in series. The lag time between the two detectors was 0.05 min. The peaks (marked ''?'') corresponding to aromatic bases visible in the DAD chromatograms can also be seen in the RI trace. Conditions as in Fig. 1.

determination of total amine content as well as the content of so-called bound amines in process liquids of amine wash developed by Chevron [7] yields correct results when the sample being analyzed contains one basic ion. However, the results are erroneous in the presence of two or more ions, e.g. MDEA and ammonium ions. Fig. 5 shows a potentiometric titration curve for a reflux sample from the desorption column (point 650 C5), the chromatogram of which is presented in Fig. 3. The insufficient selectivity of the potentiometric method with respect to amines, their degradation products and ammonium ions makes the determination of individual species impossible.

Investigations of the effect of the addition of NH_4Cl to samples containing MDEA or MEA demonstrated that the simultaneous determination of ammonium ions and an amine by the potentiometric method is impossible. Depending on the assumed conversion factor, either too high concentration of MDEA or too low concentration of ammonium ion is obtained. The studies also demonstrated that, in the case of a high concentration of MDEA in the investigated sample, point EP-2 appears at a lower pH value (about 10.2), whereas in the case of a high concentration of ammonium ion, the pH value of the end point EP-2 is higher (at about 10.8).
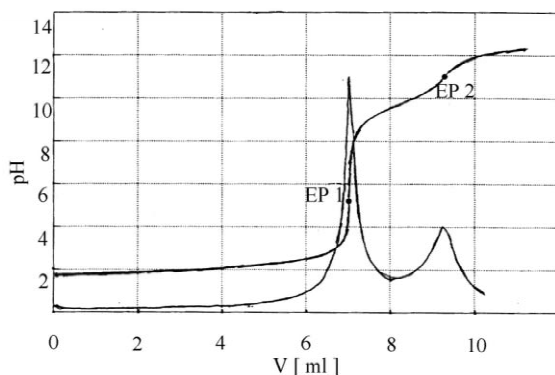

Fig. 5. Potentiometric titration curve of a sample of desorption column reflux from the amine wash installation (point 650 C5), the chromatogram of which is shown in Fig. 3. EP-1, inflection point for an excess of hydrochloric acid added to the sample; EP-2, inflection point for the sum of amines and ammonium ion. Analytical conditions: acid–base titration with ca. 0.1 *M* NaOH solution; potentiometer with a glass indicator electrode and a calomel reference electrode.

4. Conclusions

In the refining and petrochemical industries, classical acid–base titration in the presence of a visual indicator or potentiometric titration with a glass electrode as an indicator electrode [7] are traditionally used to determine the concentration of gas-treating amines MEA, DEA, MDEA, etc. However, these methods are not reliable in the presence of ammonium ions or in the case of substantial degradation of the amines due to insufficient selectivity.

The method described in this paper, utilizing cation-exchange liquid chromatography with RI detection, is sufficiently selective and sensitive for process analysis. It allows the separation and determination of the proper amine, some of its degradation products and ammonium ion. When UV (or DAD) detection is used in series with RI detection, it is possible to ensure that aromatic amines or heterocyclic nitrogen compounds do not interfere with the determination. The method is simple and rapid. The concentration of analytes in the injected sample should be brought to a range from 0.01 to 1.5% by weight.

The method also allows the simultaneous determination of Na^+, Mg^{2+}, Fe^{2+}, and Ca^{2+}, although the presence of Mg^{2+} together with Fe^{2+} and some aromatic amines at a concentration >0.01% may result in interference. The method presented in this paper has been used in the Gdańsk Refinery for over a year for the simultaneous determination of amines and ammonium ions in process liquids and wastewaters.

References

[1] A. Chackma, A. Meisen, Can. J. Chem. Eng. 75 (1997) 861.
[2] P.C. Rooney, T.R. Bacon, M.S. DuPart, in: Proceedings of the Gas Conditioning Conference, 1998, p. 335.
[3] P.C. Rooney, T.R. Bacon, M. DuPart, Hydrocarbon Processing 75 (1996) 95 (Part I); 76 (1997) 65 (Part II).
[4] Instruction Manual: Heat Stable Amine Salt Maintenance Guidelines, The DOW Chemical Company, GAS/SPEC Technology Group, Freeport, TX, USA, 1999.
[5] Dionex Solutions for Increased Productivity; An Applications Guide for Chemical Petrochemical, and Petroleum Producers, Dionex Corporation, USA (LPN 0916 10M 4/97).

[6] Laboratory Instruction, Rafineria Gdańska S.A., Wydzial NKJ, 1999 (in Polish).

[7] Analytical method: Amine Content—Titrimetric Procedure for Assaying Gas Treating Amines—CTM 5-9, Chevron Research and Technology, Richmond, CA.

[8] J.N. Lapage, E.M. Rocha, Anal. Chem. 55 (1983) 1360.

[9] K. Shimada, M. Tanaka, T. Nambare, J. Chromatogr. 280 (1983) 271.

[10] S.A. Bouyoucos, Anal. Chem. 52 (1977) 401.

[11] F.C. Smith, R.C. Chang, CRC Crit. Rev. Anal. Chem. (1980) 197.

[12] J. Vialle, M.C. Bertrand, M. Kolosky, O. Paisse, G. Raffin, Analusis 17 (1989) 376.

[13] R. Kadnar, J. Chromatogr. A 850 (1999) 289.