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Solid-phase extraction-gas chromatography and solid-phase extraction-gas chromatography–mass spectrometry determination of corrosion inhibiting long-chain primary alkyl amines in chemical treatment of boiler water in water-steam systems of power plants

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Abstract

Gas chromatography with simultaneous flame-ionization detection (FID) and a nitrogen-phosphorus detection (NPD) as well as gas chromatography–mass spectrometry (GC/MS) has been used to characterize long-chain primary alkyl amines after derivatization with trifluoroacetic anhydride (TFAA). Electron impact ionization- (EI) and negative chemical ionization (NCI) mass spectra of trifluoroacetylated derivatives of the identified *tert*-octadecylamines are presented for the first time. The corrosion inhibiting alkyl amines were applied in a water-steam circuit of energy systems in the power industry. Solid-phase extraction (SPE) with octadecyl bonded silica (C_{18}) sorbents followed by gas chromatography were used for quantification of the investigated *tert*-octadecylamines in boiler water, superheated steam and condensate samples from the power plant. The estimated values were: 89 $\mu g\,l^{-1}$ ($n = 5$, RSD = 7.8%), 45 $\mu g\,l^{-1}$ ($n = 5$, RSD = 5.4%) and 37 $\mu g\,l^{-1}$ ($n = 5$, RSD = 2.3%), respectively.

Keywords: GC-FID/NPD; GC/MS; Primary long-chain alkyl amines; Corrosion inhibitors

1. Introduction

The determination of amines is of great importance to the chemical and pharmaceutical industry as well as for environmental analysis [1]. Amines are widely used for the production of plastics and coating additives, dyes, medicines, pesticides, petroleum products additives, chemical intermediates and more recently as corrosion inhibitors in chemical treatment of boiler water in water-steam systems of power plants. Corrosion inhibitors are chemical substances which, when added in small amounts to a corrosive environment, will reduce, slow down or prevent corrosion to metal. Corrosion occurs in steam-water condensate systems due to carbonic acid attack and oxygen pitting [2]. Carbonic acid attack occurs due to CO_2, which is the breakdown product of carbonate alkalinity in the boiler, condensing with water to form H_2CO_3. This results in the "grooving" of condensate piping, which usually shows up first in leaks at threaded sections. Oxygen pitting occurs as steam condenses and the vacuum created pulls air into the system. Because of the localised nature of oxygen pitting, it can cause relatively quick failure in a condensate system. The most common method of addressing carbonic attack is through the use of neutralizing amines [2,3]. These chemicals, such as morpholine and cyclohexylamine neutralize the carbonic acid, and increase the pH of the condensate. Another method to protect the plant is the application of filming aliphatic mono-, di- or polyamines and their salts. The filming substances provide a protective barrier against both carbonic acid and oxygen. Aliphatic amines are adsorbed by the surface-active $–NH_2$ groups, which forms a chemisorptive bond with the metal surface. In order to decrease oxygen pitting, a volatile oxygen scavenger such as *N*,*N*-diethylhydroxylamine (DEHA) is also used [2,3].

Applying the ideas of green chemistry to the class of organic amines corrosion inhibitors has resulted in reduced use of many of the more toxic aromatic amines/salts and the introduction of long-chain aliphatic amines or their salts as replacement [4].

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If a filming amine and/or DEHA is used, the residual in steam and water condensate should be measured. In the case of DEHA, a residual of 100–150 μg l^{-1} is usually targeted [2].

The high polarity of the amines renders analysis with common analytical techniques difficult since the solutes are not easily extracted from the polar water matrix [5,6]. Aqueous samples have to be concentrated to meet the desired detection limits. This can be performed by liquid/liquid extraction (LLE) [7,8], solid-phase extraction (SPE) [9,10], solid-phase microextraction (SPME) [11] or sorptive extraction-thermal desorption (SE/TD) [6]. In order to reliably determine amines at low concentration levels, chromatographic analysis coupled to sensitive and selective detections is the best option to use [6]. The use of liquid chromatography (LC) requires the analytes to be derivatized since the alkyl amines have no chromophore and therefore can not be sensitively detected as such [6]. In the pre-column and the post-column derivatization of amino groups, such derivatizing reagents as 1-fluoro-2,4-dinitrobenzene [12], 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole [13] and salicylaldhyde-diphenylboron chelate [14] have been widely used to improve the HPLC determination of primary alkyl amines. Salicylaldhyde-5-sulfonate was used as derivatizing reagent for the determination of amines by capillary zone electrophoresis (CZE) [15].

Determination by capillary gas chromatography with derivatization of alkyl amines, e.g. with pentafluorobenzoyl chloride [6] or with pentafluorobenzaldehyde [16] is often preferred over LC. The most popular derivatives for GC determination of primary amines are the acetyl and the trifluoroacetyl derivatives [17,18]. The derivatization reactions for amines have been reviewed by Kataoka [19].

The purpose of this contribution was to develop a sensitive gas chromatographic method for the identification and determination of long-chain primary alkyl amines in boiler water, steam and condensate. The corrosion inhibiting alkyl amines were applied in a new technology of boiler water chemical treatment in energy systems in the power industry [20–28].

2. Experimental

2.1. Chemicals

Alkyl amines Primene JM-T^{TM} obtained from Rohm and Haas France S.A.S. (Valbonne, France) were used in our investigations.

n-Hexane for HPLC (Biosolve B.V., Valkenswaard, The Netherlands), methanol LiChrosolv gradient grade for HPLC (Merck, Darmstadt, Germany), tetrahydrofurane (THF) LiChrosolv for HPLC (Merck), dicyclohexylamine for synthesis (internal standard, Merck-Schuchardt, Hohenbrunn, Germany), trifluoroacetic anhydride (TFAA), *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA), both from Macherey-Nagel (Düren, Germany), 5% DMCS in toluene (Sylon CT) from Supelco (Bellefonte, PA, USA) and water, purity Type 1 according to the USP 25-NF 20, from a water purification system Milli-Q (Millipore Corp., Bedford, MA, USA) were used.

2.2. Samples

Spiked water samples of 10 μg l^{-1} to 100 mg l^{-1} of Primene JM-T^{TM} and water samples of boiler water, superheated steam and condensate from the Power Plant Białystok (Białystok, Poland) were investigated.

2.3. Standard solutions

For the evaluation of the quantitative determination, various standard solutions of 12.5, 25, 50, 75 and 100 mg l^{-1} Primene JM-T^{TM}-TFA with each 10 mg l^{-1} of dicyclohexylamine (internal standard, I.S.) in *n*-hexane/THF 95/5 (v/v) were prepared.

2.4. Derivatization procedure

A compact ultrasonic bath Sonorex Super RK 31H from Bandelin electronic (Berlin, Germany) and deactivated with 5% DMCS in toluene (Sylon CT) reaction vessels of 5 ml with solid cap and PTFE liner (Supelco) were used for derivatization.

Approximately 10 mg of the investigated Primene JM-T^{TM} dissolved in 0.5 ml THF in a 5 ml glass micro-reaction vessel and 100 μl of TFAA were added. The sealed vessel was placed in the ultrasonic bath and agitated by heating at 60 °C for 15 min. After the reaction had occurred, excess of reagent, released trifluoroacetic acid and THF were evaporated with a gentle steam of nitrogen at room temperature or by using a vacuum pump. The resulting product was dissolved in 1 ml of *n*-hexane or in 1 ml of THF and analyzed by GC/FID, GC/NPD and GC/MS.

2.5. Solid-phase extraction (SPE)

For solid-phase extraction of organic compounds from water samples, the following SPE sorbents were used: Superclean ENVI-18 (polymerically bonded, octadecyl, endcapped, 500 mg/3 ml) obtained from Supelco (Bellefonte, PA, USA), LiChrolut® RP-18 E (octadecyl, endcapped, 500 mg/3 ml) supplied by Merck (Darmstadt, Germany), Superclean ENVI-Chrom P (styrene/divinylbenzene copolymer, 250 mg/3 ml) obtained from Supelco, CHROMABOND® EASY (polar modified styrene/divinylbenzene copolymer, 200 mg/3 ml) obtained from Macherey-Nagel (Düren, Germany) and DPA-6S (polyamide resin, 250 mg/6 ml) supplied by Supelco. The solid-phase extractions were done using the Large-Volume-SPE-Sampler (Supelco) and a vacuum pump stand MZ 2C (Vaccubrand GmbH, Wertheim, Germany). In each extraction, methanol and water were used as conditioning solvents.

2.6. Sample treatment

To prevent adsorption of alkyl amines on the glass surface, spiked water samples of 10 μg l^{-1} to 100 mg l^{-1} of Primene JM-T^{TM} were prepared and stored at ambient temperature in a 1 l polypropylene (PP) volumetric flasks (Kartell, Noviglio, Italy).

Water samples of boiler water, superheated steam and condensate from the power plant were stored at ambient temperature in 5 l PP bags (Bürkle, Lörrach, Germany). Exactly 1 or 2 l of the investigated water sample was percolated from a 1 l PP volumetric flask (Kartell) through the SPE LiChrolut® RP-18 E cartridge at about 5 ml min^{-1}. The adsorbed organic compounds were eluted in a mixture of 5 ml *n*-hexane/THF 95/5 (v/v) and collected in a deactivated micro-reaction vessel. After elution, the solvent was evaporated with a gentle steam of nitrogen at room temperature or by using a vacuum pump. Then, the extract was derivatized by acylation according to the procedure described above. The resulting product was dissolved in 1 ml of the internal standard solution, containing 12 mg l^{-1} of dicyclohexylamine in *n*-hexane and analyzed by gas chromatography.

2.7. Instrumentation

Gas chromatographic analyses were performed on an AutoSystem gas chromatograph (PerkinElmer Instruments, Norwalk, CT, USA) equipped with a split/splitless injector at 290 °C, a flame-ionization detector (FID) and a nitrogen-phosphorus detector (NPD), both operated at 320 °C. Helium 5.0 grade (Westfalen AG, Münster, Germany) was used as a carrier gas. The helium inlet pressure was 140 kPa. The fused silica capillary column used in this investigation was 60 m × 0.25 mm I.D., film thickness 0.25 μm DB-5 ms from J&W Scientific (Folsom, CA, USA). The end of the capillary column was connected to the outlet splitter (S.G.E., Melbourne, Australia). The splitter was coupled to both detectors with two equal (200 mm × 0.22 mm) uncoated deactivated fused silica capillaries. The using of the splitter allows simultaneous detection with both FID and NPD. The oven temperature was programmed from 60 °C (1 min hold) at 6 °C min^{-1} to 280 °C (80 min hold) or from 150 °C (1 min) hold at 6 °C min^{-1} to 280 °C (hold up to 50 min). Chromatographic data were processed with TotalChrom version 6.2 software (Perkin Elmer Instruments).

GC/MS measurements were made using an ThermoQuest Trace 2000 gas chromatograph (ThermoQuest CE Instruments, Milan, Italy) interfaced to a ThermoQuest/Finnigan Voyager quadrupole mass spectrometer (ThermoQuest/Finnigan MassLab Group, Manchester UK) operated in electron impact ionization (EI) mode and negative chemical ionization (NCI) mode with an ThermoQuest Xcalibur data system, the *NIST 98* spectra library, and a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland). The fused silica capillary column, 60 m long, 0.25 mm I.D. with DB-5 ms (J&W) stationary phase, film thickness 0.25 μm was used. The temperature of column was programmed from 60 °C (1 min hold) at 6 °C min^{-1} to 280 °C (35 min hold) or from 150 °C (1 min hold) at 6 °C min^{-1} to 280 °C (35 min hold). Helium 5.0 grade (Westfalen AG) was used as a carrier gas. The constant flow of helium of 1 $\text{cm}^3\,\text{min}^{-1}$ was used during the whole analysis. The temperature of the split/splitless injector was 250 °C and the split flow was 100 $\text{cm}^3\,\text{min}^{-1}$. The transfer line temperature was 280 °C. The ion source temperature was kept at 250 °C. The ionisation occurred with a kinetic energy of the impacting electrons of 70 eV. The emission current was 250 μA. The detector voltage was 450 V. Methane grade 4.5 (Westfalen AG) was used as reagent gas for NCI. Mass spectra and reconstructed chromatograms (total ion current [TIC]) were obtained after eluting of solvent (9 min) by automatic scanning in the mass range *m*/*z* 35–450.

3. Results and discussion

3.1. Derivatization

Amines are generally known to be very difficult to analyze due to their basic character. In addition to the basic character, the amino group introduces a large dipole in the molecule. This dipole is responsible for strong interaction with silanol groups and siloxane bridges in the structure of the stationary phase of the GC capillary column. This often results in nonlinear adsorption effects and can be seen as strong tailing peaks in the chromatogram. The best way to prevent interaction of the strong dipole is to derivatize the amine. The choice of a derivatizing reagent is based on the functional group requiring derivatization, the presence of other functional groups in the molecule and the reason for performing the derivatization [18]. Our studies were conducted to establish the optimum conditions for derivatization, solid-phase extraction, chromatographic separation, identification and quantification of the investigated alkyl amines. At the beginning, possible ways of derivatization were considered. In principle, acylation, alkylation and silylation can be used for derivatization of the –NH_2 groups contained in alkyl amine structures [18,19]. Each of the possibilities has some advantages and drawbacks. First attempts in our laboratory with silylation agent MSTFA were unsatisfying. Good results from previous work of the authors [29,30] with trifluoroacetic acid and trifluoroacetic anhydride (TFAA) stimulated us to proceed with acylation. Acylation is the conversion of compounds that contain active hydrogens (–NH, –OH, –SH) into amides, esters or thioesters through the action of a carboxylic acid or carboxylic derivative. For our investigations of the long-chain alkyl amines, we have selected trifluoracetic anhydride (TFAA) as the acylation reagent. This reaction is preferred for alkyl amine derivatization [18]:

$$(\text{R}_1)(\text{R}_2)(\text{R}_3)\text{C–NH}_2 + (\text{CF}_3\text{CO})_2\text{O} \rightarrow (\text{R}_1)(\text{R}_2)(\text{R}_3)\text{C–NH–C(O)CF}_3 + \text{CF}_3\text{COOH} \quad (1)$$

3.2. Identification

Fig. 1 shows the GC/FID and GC/NPD chromatograms of trifluoroacetylated (TFA) derivative of Primene JM-T™ dissolved in *n*-hexane, while Fig. 2 shows a typical total ion current GC/MS chromatogram of the same sample. Some of the obtained EI and NCI mass spectra of the separated compounds from Primene JM-T™-TFA are shown in Figs. 3 and 4, respectively. Table 1 presents the significant *m*/*z* fragments in the recorded EI and NCI mass spectra of the investigated TFA derivatives of Primene JM-T™. Other characteristic fragments in Fig. 3 (A–G): $[\text{C}_3\text{H}_5]^+$ (*m*/*z* 41), $[\text{C}_4\text{H}_7]^+$ (*m*/*z* 55), $[\text{C}_5\text{H}_9]^+$ (*m*/*z* 69), $[\text{C}_6\text{H}_{11}]^+$ (*m*/*z* 83), $[\text{C}_7\text{H}_{13}]^+$ (*m*/*z* 97), $[\text{C}_8\text{H}_{15}]^+$ (*m*/*z* 111) and $[\text{C}_9\text{H}_{17}]^+$ (*m*/*z* 125) are formed in the McLafferty type-reaction of alkene elimination from the molecule of alkyl amine. The proposed chemical

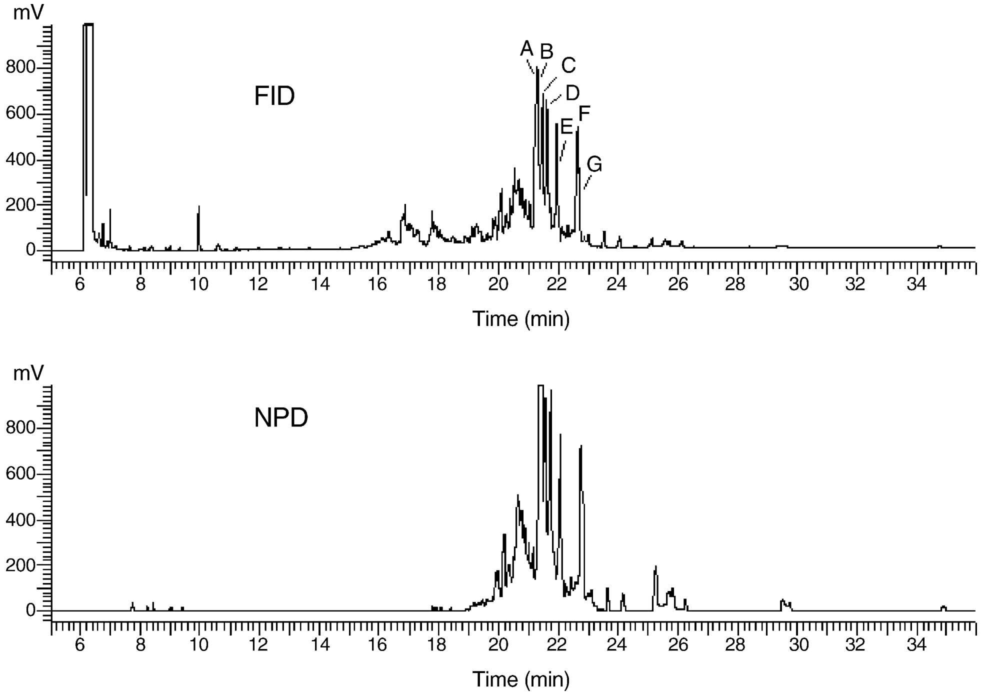

Fig. 1. GC/FID (top) and GC/NPD (bottom) chromatograms of trifluoroacetylated (TFA) derivative of Primene JM-T^{TM} dissolved in *n*-hexane. Fused silica capillary column: DB-5 ms, 60 m × 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 150 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 30 min). Split/splitless injector: 290 °C. Helium constant pressure 140 kPa, split flow 50 cm^3 min^{-1}. Peak identification: t_R = 16.3–19.0 min: isomers of octadecene; (A) t_R = 21.70 min: 8-methyl-8-heptadecaneamine-TFA; (B) t_R = 21.77 min: 7-methyl-7-heptadecaneamine-TFA; (C) t_R = 21.88 min: 6-methyl-6-hetadecaneamine-TFA; (D) t_R = 22.06 min: 5-methyl-5-heptadecaneamine-TFA; (E) t_R = 22,38 min: 4-methyl-4-heptadecaneamine-TFA; (F) t_R = 23.09 min: 3-methyl-3-heptadecaneamine-TFA; (G) t_R = 23.16 min: 2-methyl-2-heptadecaneamine-TFA.

structures of the investigated *tert*-octadecylamines are summarized in Table 1. Up to the present, there is no information in literature about mass spectra of *tert*-octadecylamines or their derivatives.

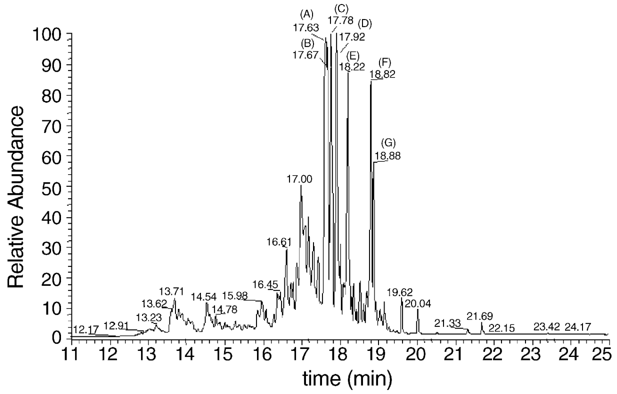

Fig. 2. Total ion current GC/MS chromatogram of trifluoroacetylated (TFA) derivative of Primene JM-T^{TM} dissolved in *n*-hexane. Fused silica capillary column: DB-5 ms, 60 m × 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 150 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 30 min). Split/splitless injector: 250 °C. Helium constant flow 1 cm^3 min^{-1}, split flow 100 cm^3 min^{-1}. Peak identification: t_R = 13.0–15.5 min: isomers of octadecene. For other peaks identification, see Table 1.

3.3. SPE process of water samples containing Primene JM-T^{TM}

Sample preparation procedures are usually the most laborious, time-consuming and critical part in the analytical process. In water analysis, the whole range of compounds of interest should be efficiently recovered from the original water sample. Solid-phase extraction (SPE) introduced in the 1970s is one of the possible techniques which may be used in the pre-concentration step of the analytical procedure [31–36]. A large number of sorbents are used for the isolation of organic compounds from the extracted solutions. They include alumina, Florisil (magnesium silicate), ion-exchange resins, polyamide resin, styrene-divinylbenzene copolymers, graphitized carbon and silica gel. Reversed-phase silica gel SPE sorbents are packing materials that are more hydrophobic than the sample. Octadecyl bonded silica (C_{18}) are the most hydrophobic silica-based SPE sorbents. They are very popular due to its strong retentive character for non-polar compounds. These sorbents are commonly used in SPE when aqueous samples are involved [32]. In our investigations, the effectiveness of the pre-concentration was evaluated for different class of SPE sorbents (see Section 2.5) using the standard solution of 100 mg l^{-1} Primene JM-T^{TM} in water. The best average SPE yield (recovery) of 61.3% ($n = 3$) Primene JM-T^{TM} was achieved using C_{18} cartridges LiChrolut® RP-18 E and *n*-hexane/THF 95/5 (v/v) as the eluent. Similar results were obtained by using Superclean ENVI-18 sorbents. For

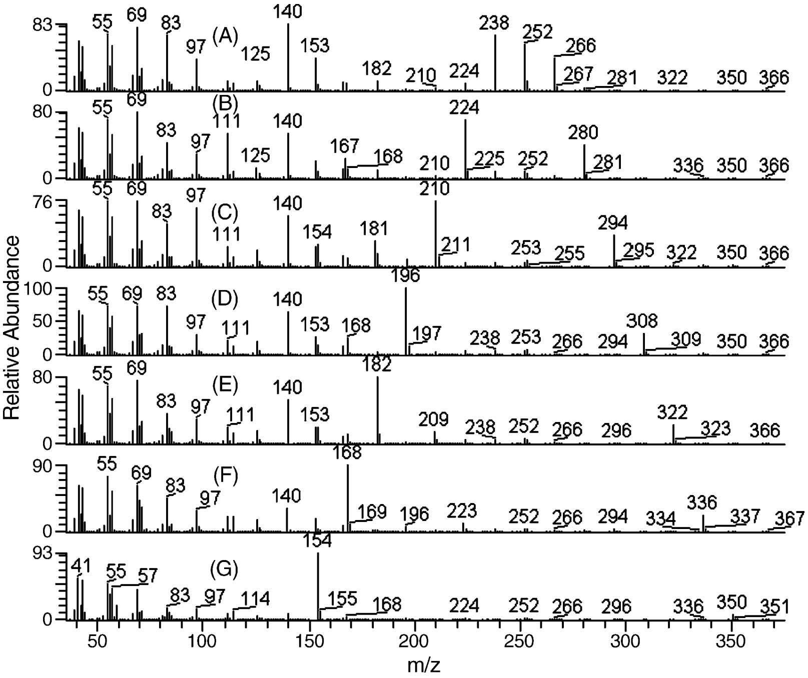

Fig. 3. Electron impact ionization (EI) mass spectra of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines identified in Primene JM-T$^{\text{TM}}$. For mass spectra identification, see Table 1.

styrene/divinylobenzene- and polyamide sorbents low recoveries (<50%) of Primene JM-T$^{\text{TM}}$ were observed. Therefore, LiChrolut$^{®}$ RP-18 E cartridges and *n*-hexane/THF 95/5 (v/v) as the eluent were further used for the SPE of boiler water, superheated steam and condensate samples from the power plant.

3.4. *Quantitative determination of Primene JM-T$^{\text{TM}}$ in water samples*

The linearity of both FID and NPD for the quantitative determination of Primene JM-T$^{\text{TM}}$ in boiler water, superheated steam and condensate samples from the power plant was evaluated by

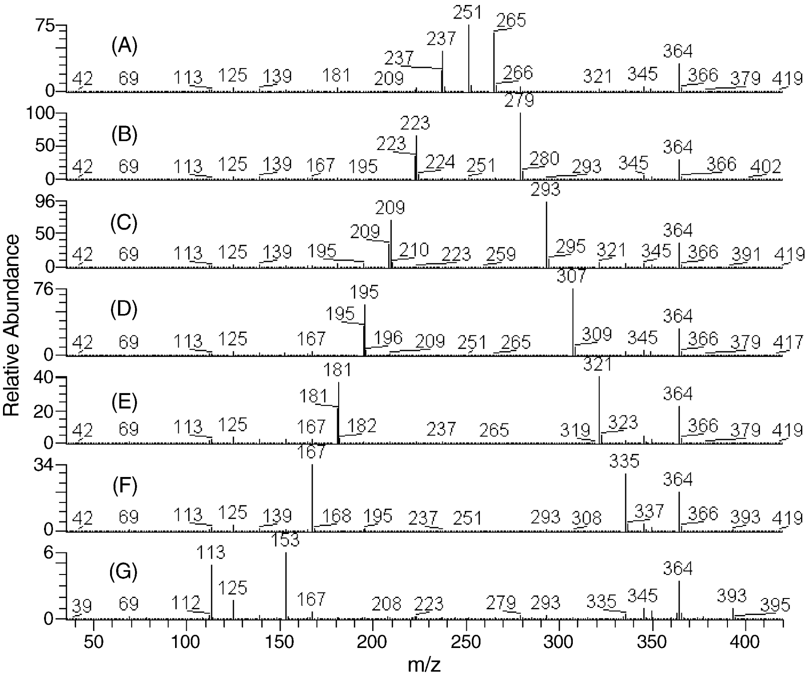

Fig. 4. Negative chemical ionization (NCI) mass spectra of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines identified in Primene JM-T$^{\text{TM}}$. For mass spectra identification, see Table 1.

Table 1
Retention data and identification of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines in Primene JM-T^{TM} (Figs. 2–4)

Peak/mass spectrum	t_R (min)	Significant fragments (*m/z*)		Proposed chemical structure
		EI	NCI	
A	17.63	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M–C_9H_{19}]^{+\bullet}$ (238); $[M–C_8H_{17}]^{+\bullet}$ (252); $[M–C_7H_{15}]^{+\bullet}$ (266);	$[M–1–C_9H_{19}]^+$ (237); $[M–1–C_8H_{17}]^+$ (251); $[M–1–C_7H_{15}]^+$ (265); $[M–1]^+$ (364);	8-Methyl-8-heptadecaneamine-TFA
B	17.67	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M–C_{10}H_{21}]^{+\bullet}$ (224); $[M–C_6H_{13}]^{+\bullet}$ (280);	$[M–1–C_{10}H_{21}]^+$ (223); $[M–1–C_6H_{13}]^+$ (279); $[M–1]^+$ (364);	7-Methyl-7-heptadecaneamine-TFA
C	17.78	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M–C_{11}H_{23}]^{+\bullet}$ (210); $[M–C_5H_{11}]^{+\bullet}$ (294);	$[M–1–C_{11}H_{23}]^+$ (209); $[M–1–C_5H_{11}]^+$ (293); $[M–1]^+$ (364);	6-Methyl-6-heptadecaneamine-TFA
D	17.92	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M–C_{12}H_{25}]^{+\bullet}$ (196); $[M–C_4H_9]^{+\bullet}$ (308);	$[M–1–C_{12}H_{25}]^+$ (195); $[M–1–C_4H_9]^+$ (307); $[M–1]^+$ (364);	5-Methyl-5-heptadecaneamine-TFA
E	18.22	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M–C_{13}H_{27}]^{+\bullet}$ (182); $[M–C_3H_7]^{+\bullet}$ (322);	$[M–1–C_{13}H_{27}]^+$ (181); $[M–1–C_3H_7]^+$ (321); $[M–1]^+$ (364);	4-Methyl-4-heptadecaneamine-TFA
F	18.82	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M–C_{14}H_{29}]^{+\bullet}$ (168); $[M–C_2H_5]^{+\bullet}$ (336);	$[M–1–C_{14}H_{29}]^+$ (167); $[M–1–C_2H_5]^+$ (335); $[M–1]^+$ (364);	3-Methyl-3-heptadecanamine-TFA
G	18.88	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M–C_{15}H_{31}]^{+\bullet}$ (154); $[M–CH_3]^{+\bullet}$ (350);	$[M–1–C_{15}H_{31}]^+$ (153); $[M–1–CH_3]^+$ (349); $[M–1]^+$ (364);	2-Methyl-2-heptadecanamine-TFA

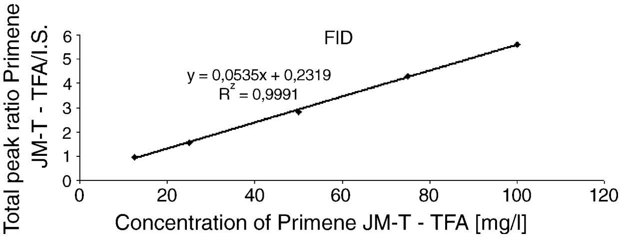

Fig. 5. Total peak area ratio Primene JM-T^{TM}-TFA/I.S. vs. concentration of Primene JM-T^{TM}-TFA in the standard solutions for FID.

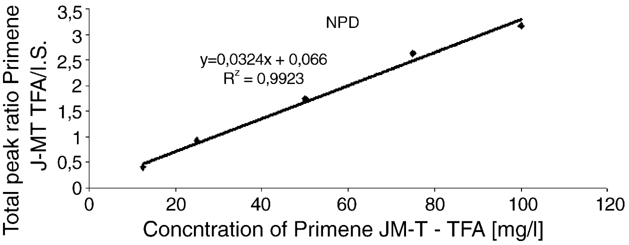

Fig. 6. Total peak area ratio Primene JM-T^{TM}-TFA/I.S. vs. concentration of Primene JM-T^{TM}-TFA in the standard solutions for NPD.

consecutive injecting of standard solutions (see Section 2.3). Each standard solution was injected in triplicate and the mean value of the total peak area ratio Primene JM-T^{TM}-TFA/I.S. was taken for construction of the calibration line. The total peak area of Primene JM-T^{TM}-TFA means the sum of all peaks area of trifluoroacetylated *tert*-octadecylamines in the sample. The calibration graphs obtained in Figs. 5 and 6 show the relationship between the obtained total peak area ratio Primene JM-T^{TM}-TFA/I.S. and the concentration of Primene JM-T^{TM}-TFA in the standard solutions for FID and NPD, respectively. The calibration line for FID (Fig. 5) was described by the equation: $y = 0.0535x + 0.2319$, where y was the total peak area ratio Primene JM-T^{TM}-TFA/I.S. and x was the concentration of Primene JM-T^{TM}-TFA in mg l^{-1}in the standard solution. The correlation coefficient (R^2) was 0.9991. The calibration line for NPD (Fig. 6) was described by the equation: $y = 0.0324x + 0.066$, where y was the total peak area ratio Primene JM-T^{TM}-TFA/I.S. and x was the concentration of Primene JM-T^{TM}-TFA in mg l^{-1} in the standard solution. The correlation coefficient (R^2) was 0.9923.

The quantity of Primene JM-T^{TM} in boiler water, superheated steam and condensate samples from the power plant was calculated from results of chromatographic analyses and results of detectors calibration using the following formula (2):

$$C_{i\,\text{sample}} = \frac{(A'_{\text{sample}} - b) \times 100\%}{a \times f \times R} \qquad (2)$$

where $C_{i\,\text{sample}}$ is the concentration (mg l^{-1}) of Primene JM-T^{TM} in the sample, A'_{sample} is the total peak area ratio Primene JM-T^{TM}-TFA/I.S. in the sample, a is the slope of the calibration line, b is the y-intercept of the calibration line, f is the pre-concentration factor (1000–2000) and R is the average SPE yield (recovery, %) of Primene JM-T^{TM} from the water sample.

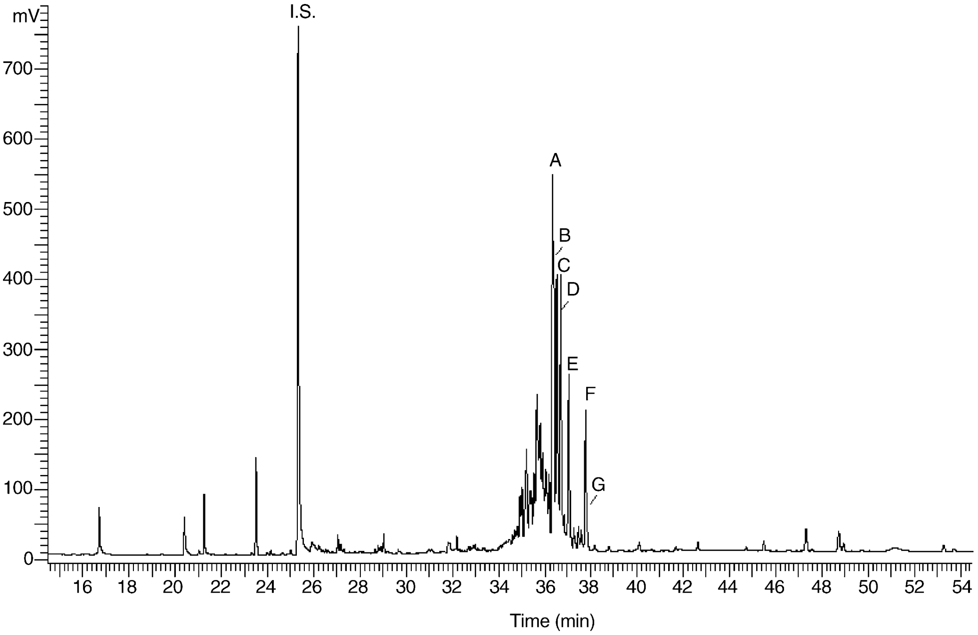

Fig. 7. SPE-GC/FID chromatogram of condensate sample from Power Plant Białystok (Poland). Fused silica capillary column: DB-5 ms, 60 m × 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 60 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 30 min). Split/splitless injector: 290 °C. Helium constant pressure 140 kPa, split flow 50 cm^3 min^{-1}. FID: 320 °C. Peak identification: (I.S.) $t_R = 25.46$ min: dicyclohexylamine (internal standard); (A) $t_R = 36.52$ min: 8-methyl-8-heptadecaneamine-TFA; (B) $t_R = 36.58$ min: 7-methyl-7-heptadecaneamine-TFA; (C) $t_R = 36.70$ min: 6-methyl-6-hetadecaneamine-TFA; (D) $t_R = 36.87$ min: 5-methyl-5-heptadecaneamine-TFA; (E) $t_R = 37.22$ min: 4-methyl-4-heptadecaneamine-TFA; (F) $t_R = 37.95$ min: 3-methyl-3-heptadecaneamine-TFA; (G) $t_R = 38.05$ min: 2-methyl-2-heptadecaneamine-TFA.

The total peak area ratio Primene JM-T$^{\mathrm{TM}}$-TFA/I.S. in the sample (A'_{sample}) was calculated from the Eq. (3):

$$A'_{\mathrm{sample}} = \frac{A_{i\,\mathrm{sample}} \times m_{\mathrm{I.S.\,sample}}}{A_{\mathrm{I.S.\,sample}} \times m_{\mathrm{I.S.\,cal}}} \qquad (3)$$

where $A_{i\,\mathrm{sample}}$ is the total peak area of all TFA derivatives of *tert*-octadecylamines in the sample, $A_{\mathrm{I.S.\,sample}}$ is the peak area of the internal standard (I.S.) in the sample, and $m_{\mathrm{I.S.\,sample}}$ and $m_{\mathrm{I.S.\,cal}}$ are the masses of the internal standard in the sample and in the standard solution used for detector calibration, respectively.

Fig. 7 shows the SPE-GC/FID chromatogram of the investigated water sample of condensate from the Power Plant Białystok (Poland). The concentrations of Primene JM-T$^{\mathrm{TM}}$ determined as the sum of *tert*-octadecylamines in samples of boiler water, superheated steam and condensate from the same power plant were: 89 μg l^{-1} ($n = 5$, RSD = 7.8%), 45 μg l^{-1} ($n = 5$, RSD = 5.4%) and 37 μg l^{-1} ($n = 5$, RSD = 2.3%), respectively.

4. Conclusion

Gas chromatography with simultaneous flame-ionization detection and a nitrogen-phosphorus detection as well as gas chromatography–mass spectrometry were successfully used for separation and identification of commercially available branched long-chain primary alkyl amines. The investigated compounds were used as corrosion inhibiting agents in water-steam circuit of energy systems in the power industry. The developed SPE-GC method with FID and NPD is suitable for the quantitative determination of trifluoroacetylated derivatives of *tert*-octadecylamines in water samples of boiler water, superheated steam and condensate from the power plant.

The presented method is well suited for the regular control of the fate of the anticorrosive agent during its practical use in water-steam circuits of the power industry.

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References

[1] J. de Zeeuw, J. Buyten, P. Heijnsdijk, R. Clarisse, Int. Laboratory (2001) 18.
[2] http://www.H$_2$Ochem.com.
[3] A. Botta, H. Graefen, D. Kuron, Werkst. Korros. 36 (1985) 407.
[4] D. Darling, R. Rakshpal, Mater. Perform. 37 (1998) 42.
[5] A. Vairavamurthy, K. Mopper, Anal. Chim. Acta 237 (1990) 237.
[6] E. Baltussen, F. David, P. Sandra, H.-G. Janssen, C. Cramers, J. High Resolut. Chromatogr. 21 (1998) 645.
[7] J. Pietsch, S. Hampel, W. Schmidt, H.-J. Brauch, E. Worch, Fresenius J. Anal. Chem. 355 (1996) 164.
[8] F. Sacher, S. Lenz, H.-J. Brauch, J. Chromatogr. A 764 (1997) 85.
[9] D. Djozan, M.A. Faraj-Zadah, J. High Resol. Chromatogr. 19 (1996) 633.
[10] W.H. Matchett, W.C. Brumley, J. Liq. Chromatogr. Relat. Technol. 20 (1997) 79.
[11] L. Pan, J.M. Chong, J. Pawliszyn, J. Chromatogr. A 773 (1997) 249.
[12] F.A.L. van der Horst, J.J.M. Holthuis, J. Chromatogr. 426 (1988) 267.

[13] A.V. Khryashchevskii, O.A. Shpigum, P.N. Nesterenko, Anal. Chem. 52 (1997) 727.

[14] K.E. Class, E. Hohaus, H. Monien, Fresenius Z. Anal. Chem. 325 (1986) 15.

[15] R. Driouich, T.T. Takayanagi, M. Oshima, S. Motomizu, J. Chromatogr. A 934 (2001) 95.

[16] K.K. Ngim, S.E. Ebeler, M.E. Lew, D.G. Crosby, J.W. Wong, J. Agric. Food Chem. 48 (2000) 3311.

[17] L.D. Metcalfe, J. Chromatogr. Sci. 13 (1975) 516.

[18] D.R. Knapp, Handbook of Analytical Derivatization Reactions, John Wiley and Sons, New York, 1979.

[19] H. Katoka, J. Chromatogr. A 733 (1996) 733.

[20] W. Jerzykiewicz, J. Hetper, M. Kozupa, R. Krupiczka, Inzynieria i Aparatura Chemiczna 34 (1995) 8.

[21] R. Krupiczka, H. Walczyk, Z. Ziobrowski, A. Rotkegel, W. Jerzykiewicz, M. Kozupa, Inzynieria i Aparatura Chemiczna 34 (1995) 22.

[22] W. Jerzykiewicz, M. Kozupa, Ochrona przed Korozją 42 (1999) 226.

[23] S. Twardowski, M. Maciejko, M. Kozupa, Energetyka (9) (2000) 75.

[24] S. Twardowski, M. Kozupa, Energetyka (3) (2002) 155.

[25] M. Kozupa, Thermal stable alkylamines Primene^{TM} as a basis for new formulation for correction of water-steam and heating water systems, Amines Workshop, 21–22.05.2002, Tarda, Poland.

[26] M. Kozupa, M. Majchrzak, W. Jerzykiewicz, New technology for boiler water chemical treatment in the energy industry, 4. Kooperationstag Chemie 2003, Fachhochschule Bonn-Rhein-Sieg, 30.09.2003, Rheinbach, Germany.

[27] M. Kozupa, M. Szymonik, J. Ścigała, S. Twardowski, M. Maciejko, Energetyka (2) (2004) 114.

[28] M. Kozupa, S. Twardowski, M. Maciejko, D. Woszczek, K. Golenia, Energetyka (9) (2004) 493.

[29] P. Welzel, G. Knupp, F.J. Witteler, T. Schubert, H. Duddeck, D. Müller, G. Höfle, Tetrahedron 37 (1981) 97.

[30] P. Kusz, H. Szewczyk, P. Król, C. Latocha, Kautschuk + Gummi, Kunststoffe 41 (1988) 48.

[31] E.M. Thurman, M.S. Mills, Solid-Phase Extraction—Principles and Practice, Wiley, Toronto, 1998.

[32] K. Bielicka, A. Voelkel, J. Chromatogr. A 918 (2001) 145.

[33] K. Luks-Betlej, P. Popp, B. Janoszka, H. Paschke, J. Chromatogr. A 938 (2001) 93.

[34] L. Brossa, R.M. Marcé, F. Borrull, E. Pocurull, J. Chromatogr. A 963 (2002) 287.

[35] D. Jahr, E. Roscher, Deutsche Lebensmittel-Rundschau 96 (2002) 403.

[36] H. Dąbrowska, Ł. Dąbrowski, M. Biziuk, J. Gaca, J. Namieśnik, J. Chromatogr. A 1003 (2003) 29.

[37] http://www.eureka.be/inaction/AcShowProject.do?id=2426.