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Chapter 5

GAS CHROMATOGRAPHIC SEPARATION AND MASS SPECTROMETRIC IDENTIFICATION OF CORROSION INHIBITING LONG-CHAIN PRIMARY ALKYL AMINES AND ALKYL DIAMINES APPLIED IN WATER TREATMENT IN THE POWER INDUSTRY

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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 some long-chain primary alkyl amines and alkyl diamines after derivatization with trifluoroacetic anhydride (TFAA).

Electron impact ionization- (EI) and chemical ionization (PCI and/or NCI) mass spectra of trifluoroacetylated derivatives of the identified long chain C_{14} – C_{20} *n*-alkyl amines, *tert*-octadecylamines and C_8 – C_{18} *N*-1-alkyl-1,3-propanediamines are presented. The corrosion inhibiting alkyl amines and alkyl diamines 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 alkyl amines and alkyl diamines in boiler water, superheated steam and condensate samples from the power plant.

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INTRODUCTION

The determination of amines is of great importance to the chemical and pharmaceutical industry as well as for environmental analysis. 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. 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. 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 provides 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. Boiler water treatment is therefore essential for both the operating efficiency and equipment live.

In agreement with the ideas of green chemistry, new types of corrosion inhibitors should be low toxic, biodegradable and soluble in aqueous medium. In the development of new inhibiting formulations, the toxic aromatic amines/salts should be replaced with the long-chain aliphatic mono-, di- or polyamines or their salts.

The purpose of the present chapter is the gas chromatographic separation and mass spectrometric identification of thermal stable long chain primary alkyl amines and long chain alkyl diamines used in the investigation of a new class of anticorrosive and antifouling formulations for water-steam and heating water systems in the power industry. The development and testing under industrial conditions of a new class of long-chain aliphatic mono- and diamines or their salts as replacement was one of the objectives of an international cooperation with partners from research institutes and industry from Poland, Lithuania, Romania, France and Germany (EUREKA project BOILTREAT E! 2426) [1]

As a partner of this RandD project our group was engaged with the analysis and the fate of these commercially available and patented corrosion inhibitors (*e.g.* Primene JM-T™, Armeen® HTD, Duomeen® CD, Duomeen® TD, Kotamina Plus!), which are applied in a boiler water-steam circuit of energy systems in the power industry in Poland.

EXPERIMENTAL

Instrumentation

Gas chromatographic analyses were performed on two gas chromatographs. The first GC was an *AutoSystem* (PerkinElmer Instruments, Norwalk, CT, U.S.A.) 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 x 0.25 mm I.D., film thickness 0.25 μm *DB-5ms* from JandW Scientific (Folsom, CA, U.S.A.). 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 x 0.22 mm) uncoated deactivated fused silica capillaries (Figure 1).

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 (PerkinElmer Instruments).

The second GC was an *Clarus 500* gas chromatograph from PerkinElmer Instruments, equipped with two split/splitless injectors at 290 °C and two flame-ionization detectors (FIDs) operated at 320 °C. Helium 5.0 grade (Westfalen AG, Münster, Germany) was used as a carrier gas. The helium inlet pressure was 120 kPa and the split flow was 20 cm^3 min^{-1}. The fused silica capillary column used in this investigation was 60 m x 0.25 mm I.D., film thickness 0.25 μm *DB-5ms* from JandW Scientific.

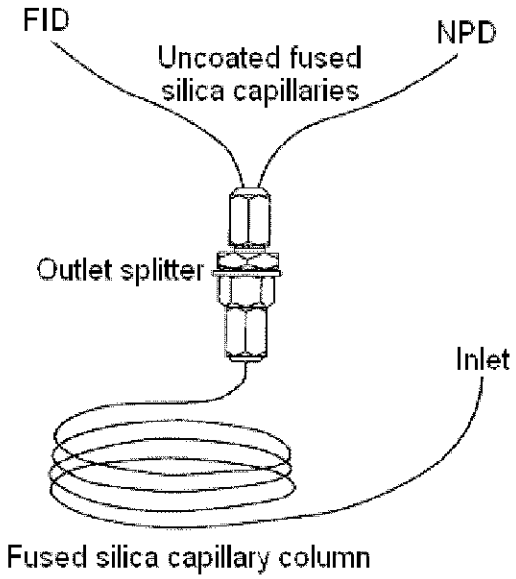


Figure 1. Simultaneous detection of long chain alkyl amines with FID and NPD after splitting the carrier gas flow on the outlet of the capillary column.

The oven temperature was programmed from 150 °C (1 min hold) at 3 °C min^{-1} to 280 °C (hold 50 min). Chromatographic data were processed with *TotalChrom Workstation* version 6.3 software (PerkinElmer Instruments).

GC/MS measurements were made using also two apparatus. The first was 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, negative chemical ionization (NCI) mode and positive chemical ionization (PCI) mode with an ThermoQuest *Xcalibur* data system, the *NIST 05* mass 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-5ms* (JandW) or *Elite-5ms* (PerkinElmer Instruments) stationary phases, film thickness 0.25 μm were used. The temperature of the column was programmed from 60 °C (1 min hold) at 3 °C min^{-1} to 280 °C (30 min hold) or from 150°C (1 min hold) at 3 °C min^{-1} to 280 °C (50 min hold). Helium 5.0 grade (Westfalen AG) was used as a carrier gas. Constant flow of helium of 1 cm^3 min^{-1} was used during the whole analysis. The temperature of the split/splitless injector was 250 °C and the split flow was 20 or 100 cm^3 min^{-1}. The transfer line temperature was 280 °C. The EI ion source temperature was kept at 250 °C. The ionization occurred with a kinetic energy of the impacting electrons of 70 eV. The emission current was 250 μA. The detector voltage was 350 V. Methane grade 4.5 (Westfalen AG) was used as reagent gas for PCI and NCI. The positive chemical ionization occurred with a kinetic energy of 70 eV. The emission current was 150 μA. The PCI ion source temperature was 250 °C. Mass spectra and reconstructed chromatograms (total ion current [TIC]) were obtained after eluting of solvent (10 min) by automatic scanning in the mass range *m/z* 35 – 750 u.

The second GC/MS was a *7890A* gas chromatograph with a series *7683B* autosampler and a series *5975C* quadrupole mass spectrometer (Agilent Technologies Inc., Santa Clara, CA, U.S.A.) operated in electron impact ionization (EI) mode. The fused silica capillary column, 30 m long, 0.25 mm I. D. with *HP-5ms* stationary phase, film thickness 0.25 μm was used. GC/MS data were processed with the *ChemStation* software (Agilent Technologies) and the *NIST 05* mass spectra library (Agilent Technologies). The temperature of the column was programmed from 150 °C (1 min hold) at 3 °C min^{-1} to 280 °C (50 min hold). Helium 5.0 grade (Westfalen AG, Münster, Germany) was used as a carrier gas. Constant flow of helium of 1.0 cm^3 min^{-1} was used during the whole analysis. The temperature of the split/splitless injector was 250 °C and the split flow was 10 cm^3 min^{-1}. The transfer line temperature was 280 °C. The EI ion source temperature was kept at 230 °C. The ionization occurred with a kinetic energy of the impacting electrons of 70 eV.

The quadrupole temperature was 150 °C. Mass spectra and reconstructed chromatograms (total ion current [TIC]) were obtained after eluting of solvent (10 min solvent delay) by automatic scanning in the mass range *m/z* 30 – 750 u.

Chemicals

Alkyl amines Armeen® HTD (hydrogenated tallow amines) (AKZO Nobel Surface Chemistry, Arnheim, The Netherlands) and Primene JM-T™ obtained from Rohm and Haas France S.A.S. (Valbonne, France), 1-hexadecylamine (90%) from ACROS ORGANICS

(Geel, Belgium), dicyclohexylamine for synthesis from Merck-Schuchardt (Hohenbrunn, Germany), alkyl diamines Duomeen® CD (*N*-cocoalkyltrimethylenediamines) and Duomeen® TD (*N*-tallowalkyltrimethylenediamines), both obtained from AKZO Nobel Surface Chemistry were used in this investigation.

n-Hexane for LC (Biosolve B.V., Valkenswaard, The Netherlands), methanol LiChrosolv gradient grade for HPLC (Merck, Darmstadt, Germany), tetrahydrofurane (THF) LiChrosolv for LC (Merck), trifluoroacetic anhydride (TFAA) from Macherey-Nagel (Düren, Germany), 5% dimethydichlorosilane (DMDCS) in toluene (Sylon CT) from Supelco (Bellefonte, PA, U.S.A.) and water purity Type 1 according to USP 25-NF 20 from the water purification system Milli-Q (Millipore Corp., Bedford, MA, U.S.A.) were used. A mixture of C_6 – C_{44} hydrocarbons in cyclohexane (ASTM D2887 Quantitative Calibration Mix) obtained from Supelco was used to calculate the retention index of each compound. For solid phase extraction of organic compounds from water samples LiChrolut RP-18 E (octadecyl, endcapped, 500 mg/3 mL) cartridges supplied by Merck were used.

Derivatization Procedure

A compact ultrasonic bath Sonorex Super RK 31H from Bandelin electronic (Berlin, Germany) and reaction vessels of 5 cm³ with solid cap and PTFE liner (Supelco) deactivated with 5% DMDCS in toluene (Sylon CT) were used for derivatization. Approximately 10 mg of the investigated alkyl amines or alkyl diamines were dissolved in 0.5 cm³ THF in a 5 cm³ 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. 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 cm³ THF and analysed by GC/MS or GC–FID–NPD.

Water Samples and Standard Solutions

Spiked water samples of 10 µg L^{-1} to 100 mg L^{-1} of Primene JM-T™ and water samples of boiler water, superheated steam and condensate from the power plant (Elektrociepłownia Białystok, Poland) were investigated. For the evaluation of the quantitative determination, various standard solutions of 12.5 mg L^{-1}, 25 mg L^{-1}, 50 mg L^{-1}, 75 mg L^{-1} and 100 mg L^{-1} Primene JM-T™-TFA with each 10 mg L^{-1} of dicyclohexylamine (internal standard, I.S.) in *n*-hexane/THF 95/5 (v/v) were prepared.

Solid-Phase Extraction (SPE) of Water Samples

Solid phase extraction (SPE) is a form of digital (step-wise) chromatography designed to extract, partition, and/or adsorb one or more components from a liquid phase (sample) onto stationary phase (sorbent or resin). Over the last twenty years, SPE has become the most powerful technique available for rapid and selective sample preparation prior to analytical chromatography. SPE extends a chromatographic systems lifetime, improves qualitative and

quantitative analysis, and by changing an analyte of interests from original matrix environment to a simpler matrix more suitable for subsequent analysis [2]. Figure 2 illustrates the four-steps of the SPE process.

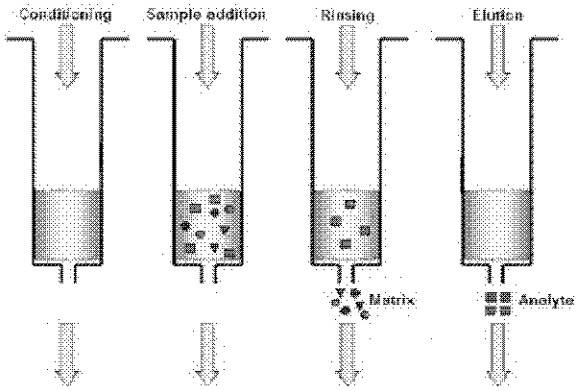


Figure 2. Illustration of the four-steps of the solid-phase microextraction (SPE) process.

To prevent adsorption of alkyl amines and alkyl diamines on the glass surface, spiked water samples of 10 μg L^{-1} to 100 mg L^{-1} of Primene JM-T™ 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 a 5 L PP bags (Bürkle, Lörrach, Germany) and extracted by solid-phase extraction (SPE) from a 1 L PP volumetric flask (Kartell). To condition the SPE LiChrolut® RP-18 E cartridge packing, the tube was rinsed with 6 cm^3 methanol followed with 6 cm^3 deionised water. After the conditioning step 1 – 2 L of the investigated water sample were percolated at a flow rate of 5 cm^3 min^{-1} through the SPE tube. After washing the tube with 5 cm^3 deionised water, the adsorbed organic compounds were eluted in a mixture of 5 cm^3 *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 cm^3 of the internal standard solution, containing 10 – 12 mg L^{-1} of dicyclohexylamine in *n*-hexane and analyzed by GC-FID-NPD.

RESULTS AND DISCUSSION

Derivatization of Alkyl Amines and Alkyl Diamines

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 [3]. The best way to prevent interaction of the strong dipole is to derivatize the amine.

Derivatization reduces the polarity of the molecule making it more retentive in chromatographic analysis. The conversion of compounds enhances GC performance as the analyte volatility is increased and peak shape improved because of reduced surface adsorption [3]. Derivatized analyte offer a greater response to the chromatographic detection system than the parent compound. 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. We have selected the acylation with trifluoroacetic acid anhydride (TFAA) as derivatization method for alkyl amines and alkyl diamines. Acylation, an alternative to silylation, is the conversion of compounds with active hydrogen such as –OH, –SH, and –NH into esters, thioesters and amides. A benefit of acylation is the formation of fragmentation-directing derivatives for GC/MS analysis.

The general reactions for acylation of the investigated alkyl amines and alkyl diamines with TFAA are shown in equations 1–3.

$$R\text{-}NH_2 + (CF_3CO)_2O \rightarrow R\text{-}NH\text{-}C(O)CF_3 + CF_3COOH \quad (1)$$

$$(R_1)(R_2)(R_3)C\text{-}NH_2 + (CF_3CO)_2O \rightarrow (R_1)(R_2)(R_3)C\text{-}NH\text{-}C(O)CF_3 + CF_3COOH \quad (2)$$

$$R\text{-}NH\text{-}(CH_2)_3\text{-}NH_2 + (CF_3CO)_2O \rightarrow R\text{-}N(COCF_3)\text{-}(CH_2)_3\text{-}NH\text{-}(COCF_3) + H_2O \quad (3)$$

Structure Elucidation of Long-Chain Primary *n*-Alkyl Amines of the Armeen® HTD-type

Figure 3 shows the GC/FID and GC/NPD chromatograms of trifluoroacetylated derivative of Armeen® HTD (hydrogenated tallow amine) in THF, while Figure 4 shows the total ion current GC/MS chromatogram of the same sample. The mass spectra formed by the electron-impact ionization of the trifluoroacetylated *n*-alkyl amines (C_{14} – C_{20}) identified in Armeen® HTD are presented in Figure 5 [4, 6]. The characteristic fragments at *m/z* 240, 254, 268, 282, 296, 310 and 324 in the mass spectra (Figure 5 A–G) are formed by the loss of the CF_3-radical of 1-aminotetradecane-TFA, 1-aminopentadecane-TFA, 1-aminohexadecane-TFA, 1-aminoheptadecane-TFA, 1-aminooctadecane-TFA, 1-aminononadecane-TFA and 1-aminoeicosane-TFA ions, respectively (equation 4).

$$[RCH_2N(H)C(O)CF_3]^{+\bullet} \rightarrow \underset{[M-69]^+}{[RCH_2N(H)CO]^+} + {}^{\bullet}CF_3 \quad (4)$$

where R = $C_{13}H_{27} \div C_{19}H_{39}$.

The peaks at *m/z* 241, 255, 269, 283, 297, 311 and 325 (Figure 5 A–G) are probably due to the suitable $[M + H - CF_3]^+$ ions. The peak at *m/z* 69 represents the $[CF_3]^+$ ion.

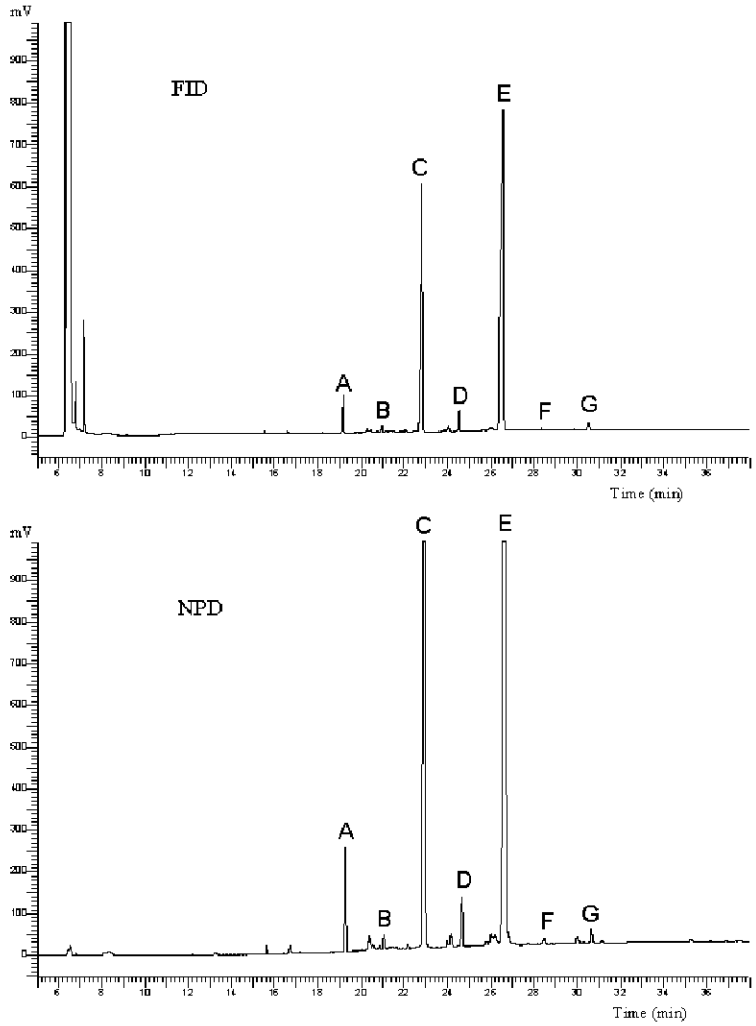


Figure 3. GC/FID (top) and GC/NPD (bottom) chromatograms of trifluoroacetylated (TFA) derivative of Armeen® HTD dissolved in THF. Fused silica capillary column: *DB-5ms*, 60 m x 0.25 mm I.D., film thickness 0.25 µm. Column temperature programmed from 150 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 30 min). Split/splitless injector: 290 °C. Helium constant pressure 140 kPa, split flow 50 cm^3 min^{-1}. Peak identification: (A) 1-aminotetradecane-TFA (t_R = 19.17 min, I_p = 1841), (B) 1-aminopentadecane-TFA (t_R = 20.95 min, I_p = 1940), (C) 1-aminohexadecane-TFA (t_R = 22.82 min, I_p = 2041), (D) 1-aminoheptadecane-TFA (t_R = 24.54 min, I_p = 2137), (E) 1-aminooctadecane-TFA (t_R = 26.57 min, I_p = 2246), (F) 1-aminononadecane-TFA (t_R = 28.33 min, I_p = 2342), (G) 1-aminoeicosane-TFA (t_R = 30.53 min, I_p = 2434). I_p – retention index in temperature-programmed gas-liquid chromatography.

The mass spectra (Figure 5 A, C and E) exhibit also a series of fragments at *m/z* 126, 140, 154, 168, 182, 196, 210, 224, 238, 252, 266, 280 and 294. They are formed in the alkyl cleavage mechanism of 1-aminotetradecane-TFA, 1-aminohexadecane-TFA and 1-aminooctadecane-TFA, respectively with a ring formation reaction, producing a series of $[(H_2C)_nNHC(O)CF_3]^+$ (n = 2 – 13) fragments with the positively charged nitrogen, and abstracting an alkyl radical.

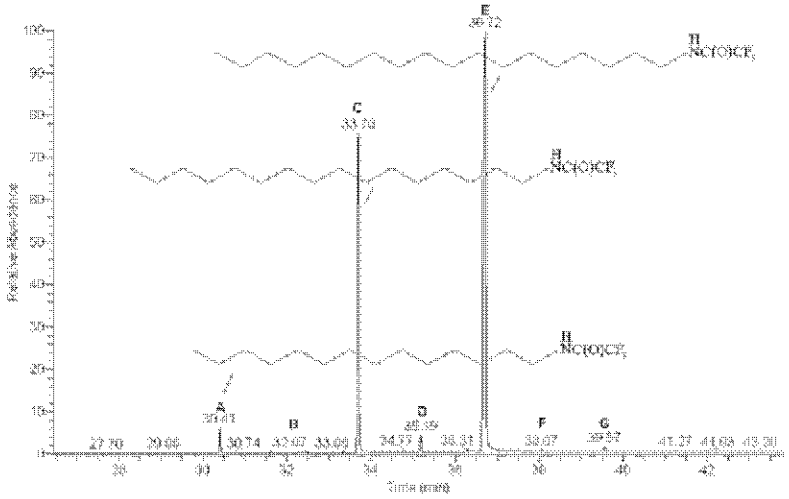


Figure 4. Total ion current GC/MS chromatogram of trifluoroacetylated (TFA) derivative of Armeen® HTD dissolved in THF. Fused silica capillary column: *DB-5ms*, 60 m x 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 60 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 35 min). Split/splitless injector: 250 °C. Helium constant flow 1 cm^3 min^{-1}, split flow 100 cm^3 min^{-1}. Peak identification: (A) 1-aminotetradecane-TFA (t_R = 30.41 min), (B) 1-aminopentadecane-TFA (t_R = 32.07 min), (C) 1-aminohexadecane-TFA (t_R = 33.70 min), (D) 1-aminoheptadecane-TFA (t_R = 35.19 min), (E) 1-aminooctadecane-TFA (t_R = 36.72 min), (F) 1-aminononadecane-TFA (t_R = 38.07 min), (G) 1-aminoeicosane-TFA (t_R = 39.57 min).

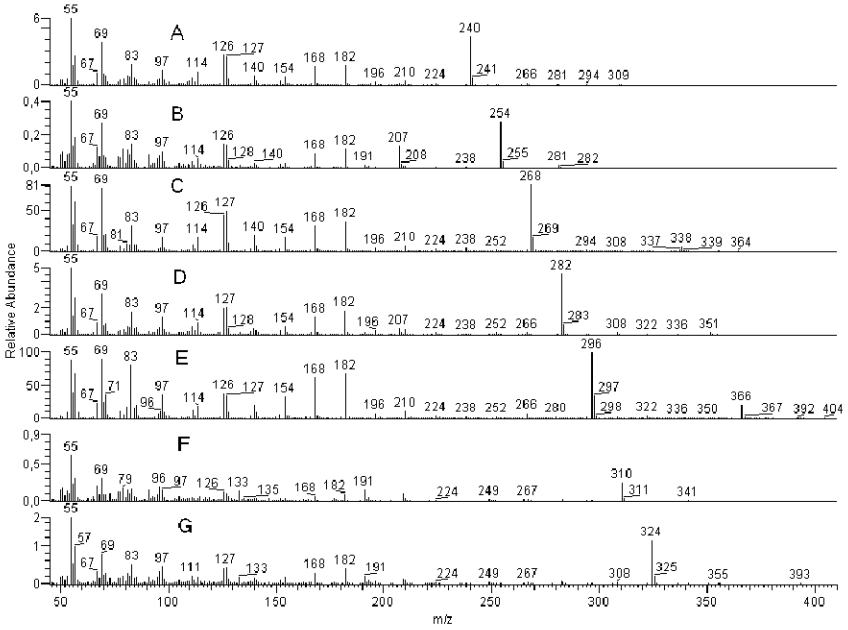


Figure 5. Electron impact ionization (EI) mass spectra of *n*-alkyl amines identified in hydrogenated tallow amine Armeen® HTD. Mass spectra identification: (A) 1-aminotetradecane-TFA; (B) 1-aminopentadecane-TFA; (C) 1-aminohexadecane-TFA; (D) 1-aminoheptadecane-TFA; (E) 1-aminooctadecane-TFA; (F) 1-aminononadecane; (G) 1-aminoeicosane-TFA.

The fragment at *m/z* 126 corresponds to the $[(H_2C)N(H)C(O)CF_3]^+$ ion from the β-cleave of the trifluoroacetylated derivatives of the alkyl amines (equation 5).

$$[RCH_2N(H)C(O)CF_3]^{+\bullet} \rightarrow \underset{m/z\ 126}{[CH_2N(H)C(O)\,CF_3]^+} + {}^{\bullet}R \qquad (5)$$

where $R = C_{13}H_{27} \div C_{19}H_{39}$.

Other characteristic fragments in Figure 5: $[C_4H_7]^+$ (*m/z* 55), $[C_5H_9]^+$ (*m/z* 69), $[C_6H_{11}]^+$ (*m/z* 83), $[C_7H_{13}]^+$ (*m/z* 97) and $[C_8H_{15}]^+$ (*m/z* 111) are formed in the McLafferty type-reaction of alkene elimination from the *N*-(alkylo)-trifluoroacetamide ions. The peak at *m/z* = 114 is due to the $[F_3CC(OH)NH_2]^+$ ion. The proposed EI-MS fragmentation pattern for *N*-(1-octadecyl)-trifluoroacetamide is shown in Figure 6 [4, 6].

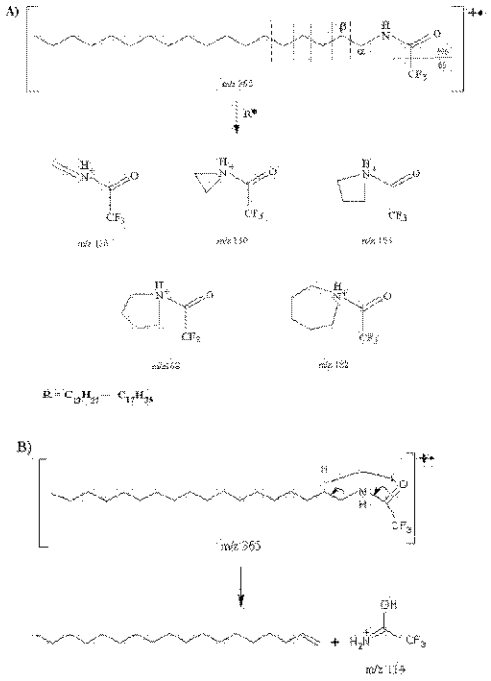


Figure 6. Proposed EI-MS fragmentation pattern for *N*-(1-ocadecyl)-trifluoroacetamide. A) Cleavage mechanism, B) McLafferty rearrangement. For mass spectrum, see Figure 5 (E).

Figure 7 shows the mass spectra obtained by the positive chemical ionization (PCI) of the trifluoroacetylated *n*-alkyl amines (C_{14} – C_{20}) identified in Armeen® HTD [4, 6]. The quasi-molecular ions $[M + H]^+$ (*m/z* 310, 324, 338, 352, 366, 380 and 394) in Figure 7 (A–G) corresponds to 1-aminotetradecane-TFA, 1-aminopentadecane-TFA, 1-aminohexadecane-TFA, 1-aminoheptadecane-TFA, 1-aminooctadecane-TFA, 1-aminononadecane-TFA and 1-aminoeicosane-TFA, respectively.

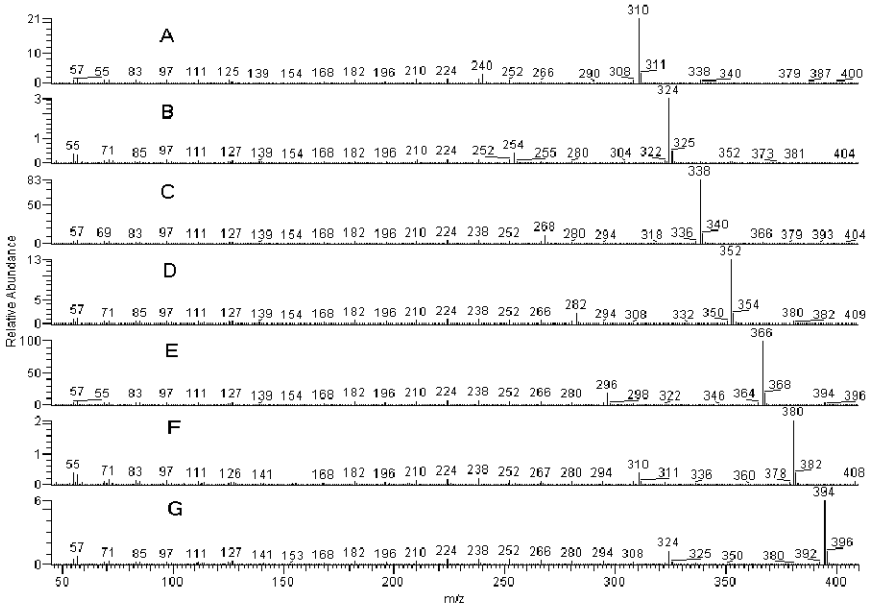


Figure 7. Positive chemical ionization (PCI) mass spectra of *n*-alkyl amines identified in hydrogenated tallow amine Armeen® HTD. Mass spectra identification: (A) 1-aminotetradecane-TFA; (B) 1-aminopentadecane-TFA; (C) 1-aminohexadecane-TFA; (D) 1-aminoheptadecane-TFA; (E) 1-aminooctadecane-TFA; (F) 1-aminononadecane; (G) 1-aminoeicosane-TFA.

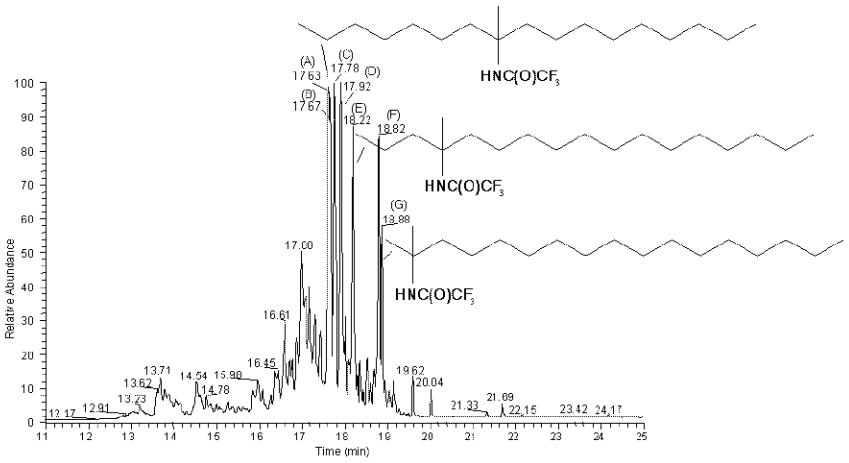


Figure 8. Total ion current GC/MS chromatogram of trifluoroacetylated (TFA) derivative of Primene JM-T™ dissolved in *n*-hexane. Fused silica capillary column: *DB-5ms*, 60 m x 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 150 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 30 min). Split/splitless injector: 250 °C. Helium constant flow of 1 cm^3 min^{-1}, split flow 100 cm^3 min^{-1}. Peak identification: t_R = 13.0 min – 15.5 min: isomers of octadecene, (A) t_R = 17.63 min: 8-methyl-8-heptadecaneamine-TFA; (B) t_R = 17.67 min: 7-methyl-7-heptadecaneamine-TFA; (C) t_R = 17.78 min: 6-methyl-6-heptadecaneamine-TFA; (D) t_R = 17.92 min: 5-methyl-5-heptadecaneamine-TFA; (E) t_R = 18.22 min: 4-methyl-4-heptadecaneamine-TFA; (F) t_R = 18.82 min: 3-methyl-3-heptadecaneamine-TFA; (G) t_R = 18.88 min: 2-methyl-2-heptadecaneamine-TFA.

Table 1. Significant fragments and identification of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines in Primene JM-T™ (Figures 9-11)

Mass spectrum	Significant fragments (*m/z*)			Chemical structure
	EI	NCI	PCI	
A	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M - C_9H_{19}]^+$ (238); $[M - C_8H_{17}]^+$ (252); $[M - C_7H_{15}]^+$ (266);	$[M - 1 - C_9H_{19}]^-$ (237); $[M - 1 - C_8H_{17}]^-$ (251); $[M - 1 - C_7H_{15}]^-$ (265); $[M - 1]^-$ (364);	$[M + H - C_9H_{20}]^+$ (238); $[M + H - CF_3C(O)NH_2]^+$ (253); $[M + H - C_7H_{16}]^+$ (266); $[M + H - CH_4]^+$ (350); $[M - H]^+$ (364); $[M + H]^+$ (366);	8-Methyl-8-heptadecaneamine-TFA
B	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M - C_{10}H_{21}]^+$ (224); $[M - C_6H_{13}]^+$ (280);	$[M - 1 - C_{10}H_{21}]^-$ (223); $[M - 1 - C_6H_{13}]^-$ (279); $[M - 1]^-$ (364);	$[M + H - C_{10}H_{22}]^+$ (224); $[M + H - CF_3C(O)NH_2]^+$ (253); $[M + H - C_6H_{14}]^+$ (280); $[M + H - CH_4]^+$ (350); $[M - H]^+$ (364); $[M + H]^+$ (366);	7-Methyl-7-heptadecaneamine-TFA
C	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M - C_{11}H_{23}]^+$ (210); $[M - C_5H_{11}]^+$ (294);	$[M - 1 - C_{11}H_{23}]^-$ (209); $[M - 1 - C_5H_{11}]^-$ (293); $[M - 1]^-$ (364);	$[M + H - C_{11}H_{24}]^+$ (210); $[M + H - CF_3C(O)NH_2]^+$ (253); $[M + H - C_5H_{12}]^+$ (294); $[M + H - CH_4]^+$ (350); $[M - H]^+$ (364); $[M + H]^+$ (366);	6-Methyl-6-heptadecaneamine-TFA
D	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M - C_{12}H_{25}]^+$ (196); $[M - C_4H_9]^+$ (308);	$[M - 1 - C_{12}H_{25}]^-$ (195); $[M - 1 - C_4H_9]^-$ (307); $[M - 1]^-$ (364);	$[M + H - C_{12}H_{26}]^+$ (196); $[M + H - CF_3C(O)NH_2]^+$ (253); $[M + H - C_4H_{10}]^+$ (308); $[M + H - CH_4]^+$ (350); $[M - H]^+$ (364); $[M + H]^+$ (366);	5-Methyl-5-heptadecaneamine-TFA
E	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M - C_{13}H_{27}]^+$ (182); $[M - C_3H_7]^+$ (322);	$[M - 1 - C_{13}H_{27}]^-$ (181); $[M - 1 - C_3H_7]^-$ (321); $[M - 1]^-$ (364);	$[M + H - C_{13}H_{28}]^+$ (182); $[M + H - CF_3C(O)NH_2]^+$ (253); $[M + 1 - C_3H_8]^+$ (322); $[M + H - CH_4]^+$ (350); $[M - H]^+$ (364); $[M + H]^+$ (366);	4-Methyl-4-heptadecaneamine-TFA
F	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M - C_{14}H_{29}]^+$ (168); $[M - C_2H_5]^+$ (336);	$[M - 1 - C_{14}H_{29}]^-$ (167); $[M - 1 - C_2H_5]^-$ (335); $[M - 1]^-$ (364);	$[M + H - C_{14}H_{30}]^+$ (168); $[M + H - CF_3C(O)NH_2]^+$ (253); $[M + H - C_2H_6]^+$ (336); $[M + H - CH_4]^+$ (350); $[M - H]^+$ (364); $[M + H]^+$ (366);	3-Methyl-3-heptadecaneamine-TFA
G	$[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCHCH_3]^+$ (140); $[M - C_{15}H_{31}]^+$ (154); $[M - CH_3]^+$ (350);	$[M - 1 - C_{15}H_{31}]^-$ (153); $[M - 1 - CH_3]^-$ (349); $[M - 1]^-$ (364);	$[M + H - C_{15}H_{32}]^+$ (154); $[M + H - CF_3C(O)NH_2]^+$ (253); $[M + H - CH_4]^+$ (350); $[M - H]^+$ (364); $[M + H]^+$ (366);	2-Methyl-2-heptadecaneamine-TFA

The characteristic fragments at *m/z* 240, 254, 268, 282, 296, 310 and 324 in the mass spectra (Figure 7 A–G) are formed, as in the case of electron-impact ionization of Armeen® HTD, by the loss of the CF_3-radical of 1-aminotetradecane-TFA, 1-aminopentadecane-TFA, 1-aminohexadecane-TFA, 1-aminoheptadecane-TFA, 1-aminooctadecane-TFA, 1-aminononadecane-TFA and 1-aminoeicosane-TFA, respectively [4, 6].

Structure Elucidation of Long-Chain Primary *iso*-Alkyl Amines of the Primene JM-T™-Type

Figure 8 shows a typical total ion current GC/MS chromatogram of trifluoroacetylated (TFA) derivative of Primene JM-T™ dissolved in *n*-hexane. The obtained EI mass spectra of the separated compounds from Primene JM-T™-TFA are shown in Figure 9 [3].

Figures 10 and 11 show the mass spectra recorded in the negative chemical ionization mode (NCI) and in the positive ionization (PCI) mode, respectively [3-4]. Table 1 presents the significant *m/z* fragments in the recorded mass spectra of the investigated TFA derivative of Primene JM-T™ [3, 8]. Other characteristic fragments in Figure 9 (A–G): $[C_3H_5]^+$ (*m/z* 41), $[C_4H_7]^+$ (*m/z* 55), $[C_5H_9]^+$ (*m/z* 69), $[C_6H_{11}]^+$ (*m/z* 83), $[C_7H_{13}]^+$ (*m/z* 97), $[C_8H_{15}]^+$ (*m/z* 111) and $[C_9H_{17}]^+$ (*m/z* 125) are formed in the McLafferty type-reaction of alkene elimination from the molecule of alkyl amine.

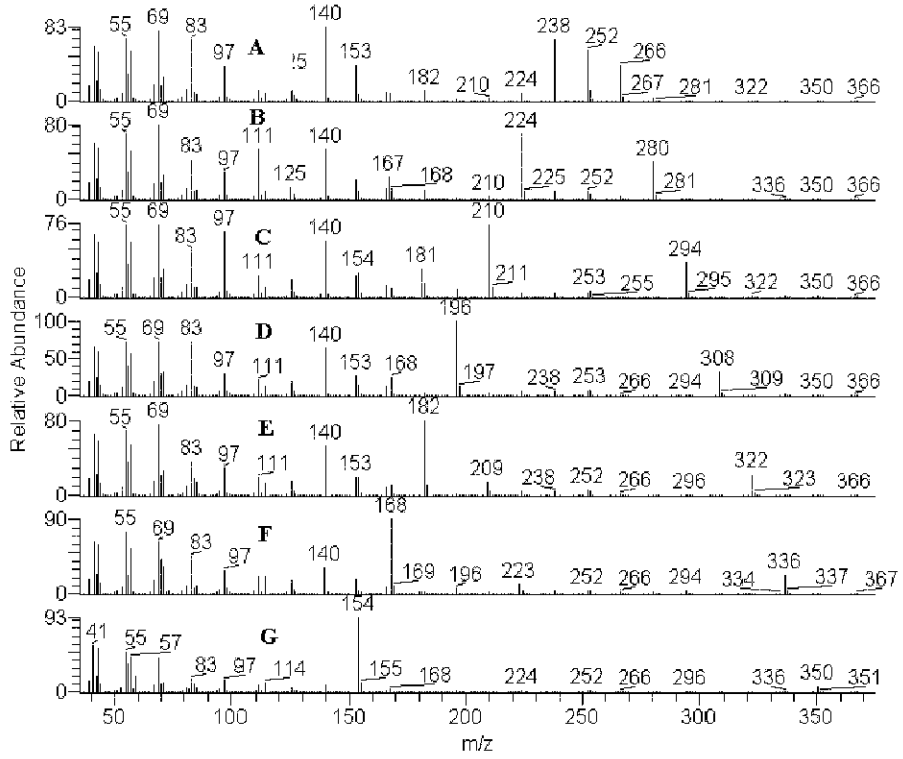


Figure 9. Electron impact ionization (EI) mass spectra of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines identified in Primene JM-T™. For mass spectra identification, see Table 1.

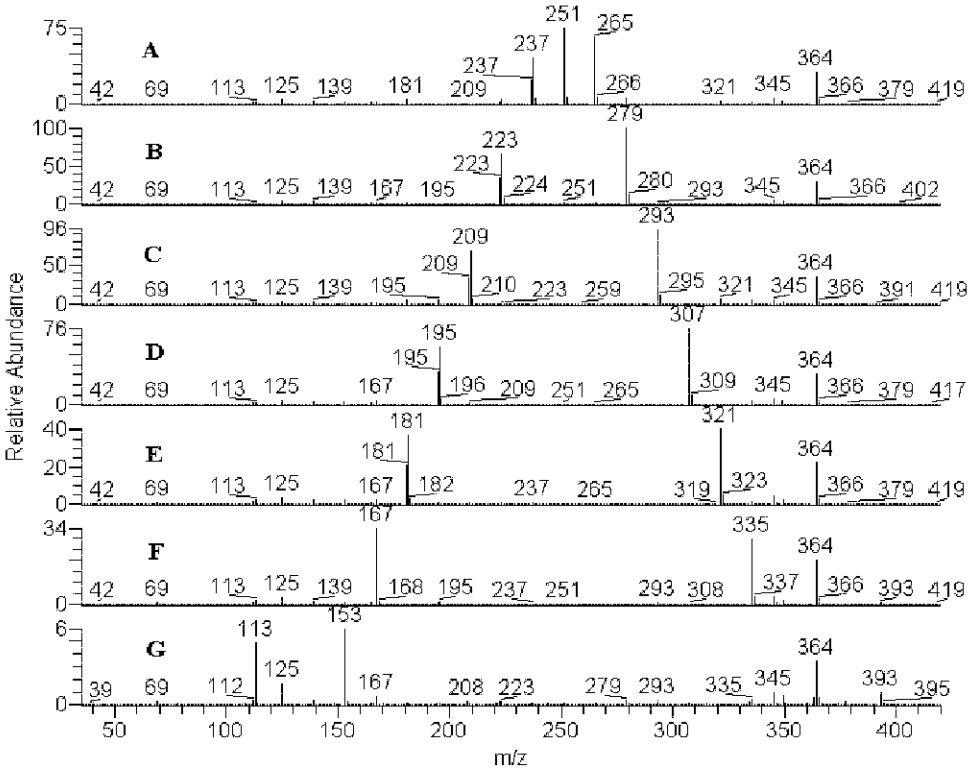


Figure 10. Negative chemical ionization (NCI) mass spectra of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines identified in Primene JM-T™. For mass spectra identification, see Table 1.

The compounds were also detected in the positive chemical ionization mode (PCI) by their quasi-molecular ions $[M + H]^+$ (*m/z* 366), $[M - H]^+$ (*m/z* 364), and by appropriate fragments (Figure 11, Table 1).

All mass spectra in Figure 11 exhibit characteristic alkyl ions: $[C_4H_9]^+$ (*m/z* 57), $[C_5H_{11}]^+$ (*m/z* 71), $[C_6H_{13}]^+$ (*m/z* 85), $[C_7H_{15}]^+$ (*m/z* 99), $[C_8H_{17}]^+$ (*m/z* 113), $[C_9H_{19}]^+$ (*m/z* 127), $[C_{10}H_{21}]^+$ (*m/z* 141), $[C_{11}H_{23}]^+$ (*m/z* 155), $[C_{12}H_{25}]^+$ (*m/z* 169), $[C_{13}H_{27}]^+$ (*m/z* 183), $[C_{14}H_{29}]^+$ (*m/z* 197) and $[C_{15}H_{31}]^+$ (*m/z* 211) differing by 14 u, formed through a cleavage mechanism of the alkyl chain of the branched alkyl amine TFA-derivatives.

The characteristic fragments at *m/z* 253 in Figure 11 corresponds to the $(R_1)(R_2)(CH_3)C^+$ carbocations, where $R_1 = CH_3 \div C_8H_{17}$, $R_2 = C_8H_{17} \div C_{15}H_{31}$ and $R_1 + R_2 = C_{16}H_{33}$, formed through a cleavage mechanism of the quasi-molecular ions $[M + 1]^+$ (Figure 12) [4]. Other characteristic fragments in Figure 11 at *m/z* 114 are formed in the McLafferty type-reaction of alkene elimination from the *N*-(*tert*-octadecylo)-trifluoroacetamide ions (Figure 12).

The McLafferty rearrangement is common for carbonyl compounds such as ketones, carboxylic acids and esters or amides. The proposed PCI fragmentation pattern for *N*-(*tert*-octadecylo)-trifluoroacetamide is shown in Figure 12 [4]. The proposed chemical structures of the investigated *tert*-octadecylamines are summarized in Table 1 [3, 8].

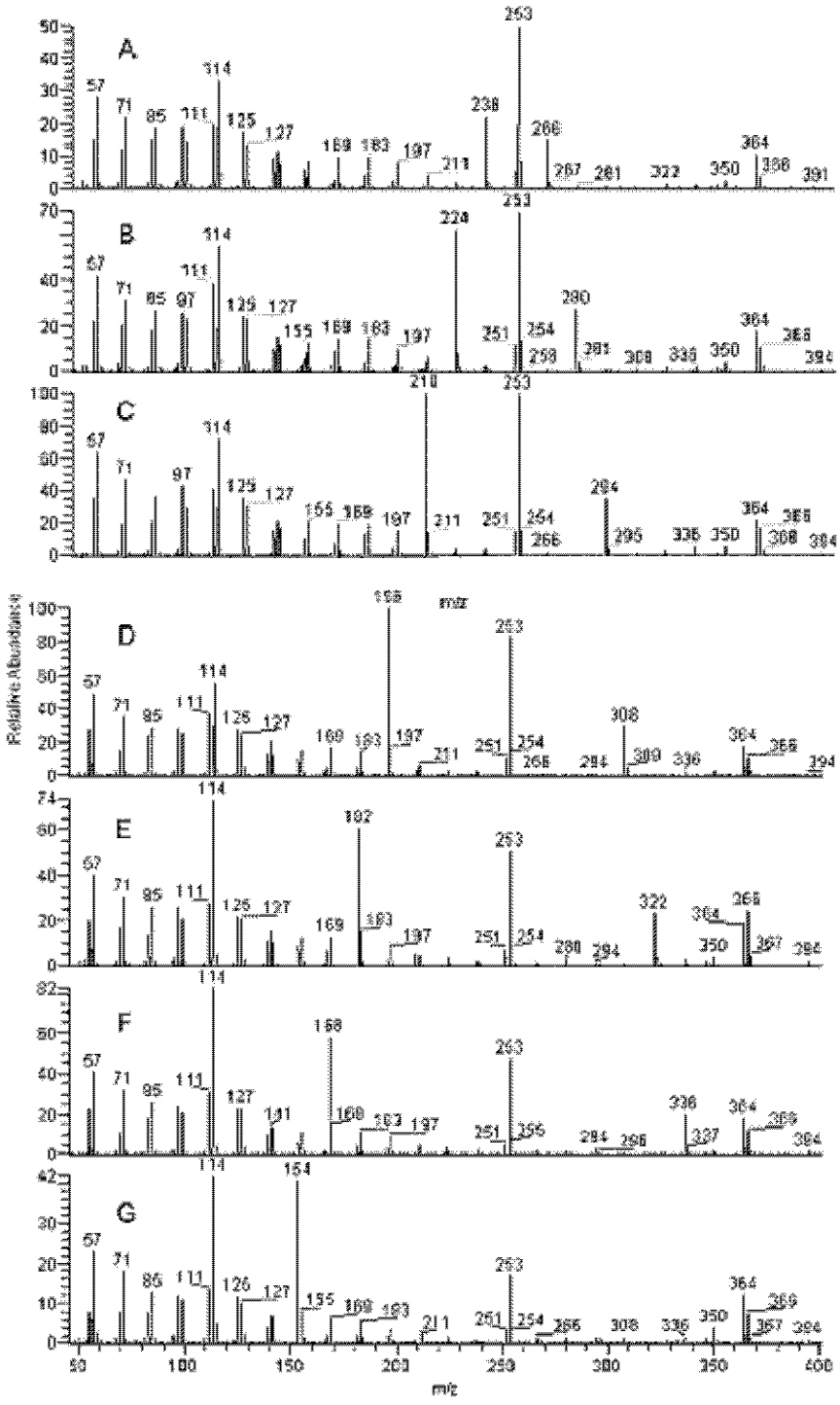


Figure 11. Positive chemical ionization (PCI) mass spectra of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines identified in Primene JM-T™. For mass spectra identification, see Table 1.

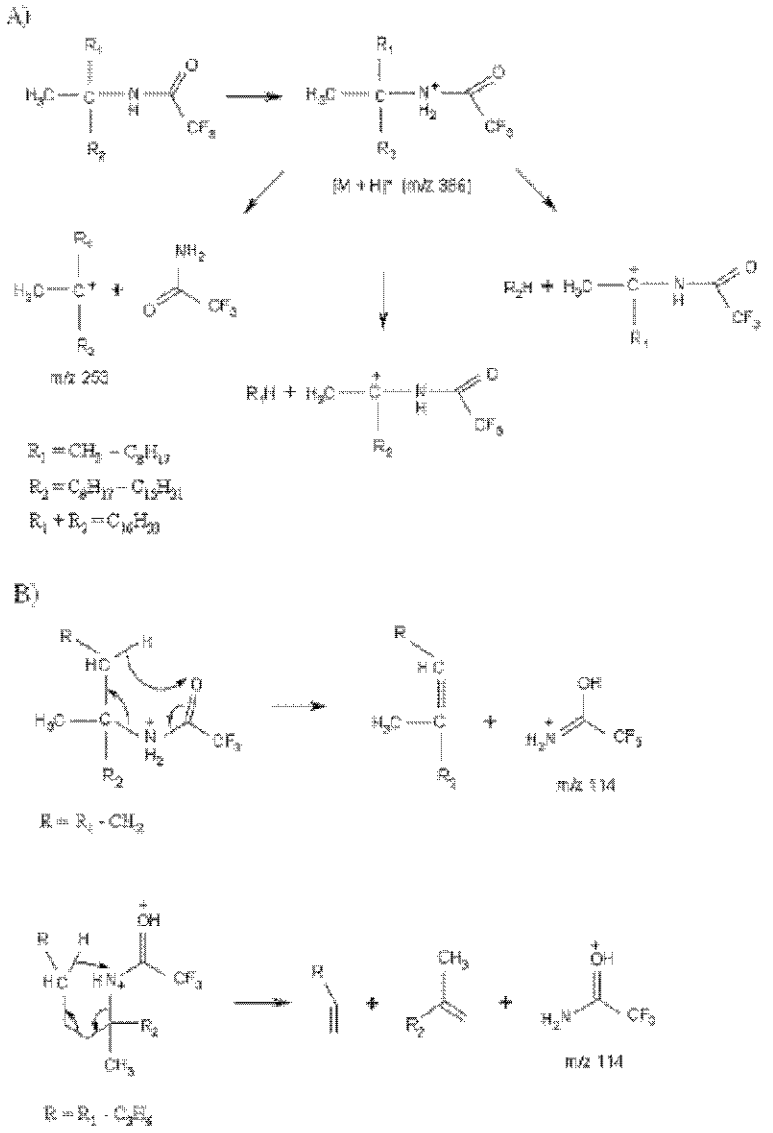


Figure 12. Proposed PCI-MS fragmentation pattern for investigated *N*-(*tert*-octadecyl)-trifluoroacetamides. A) Cleavage mechanism, B) McLafferty rearrangement. For mass spectra, see Figure 11.

Structure Elucidation of Long-Chain Primary Alkyl Diamines of the Duomeen®-Type

Figure 13 shows the chromatograms of both trifluoroacetylated derivatives of *N*-cocoalkyltrimethylenediamines (Duomeen® CD) and *N*-tallowalkyltrimethylenediamines (Duomeen® TD) obtained with the *HP-5ms* capillary column, while the retention times of the separated compounds are contained in the description of Figure 13.

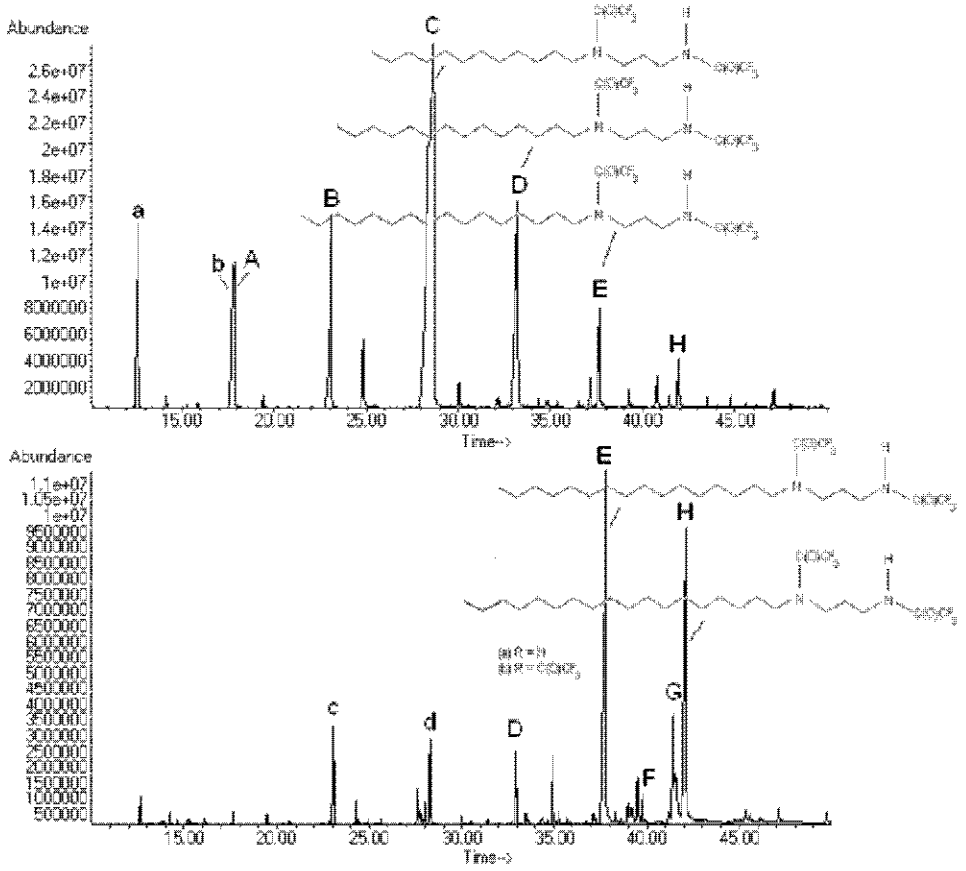
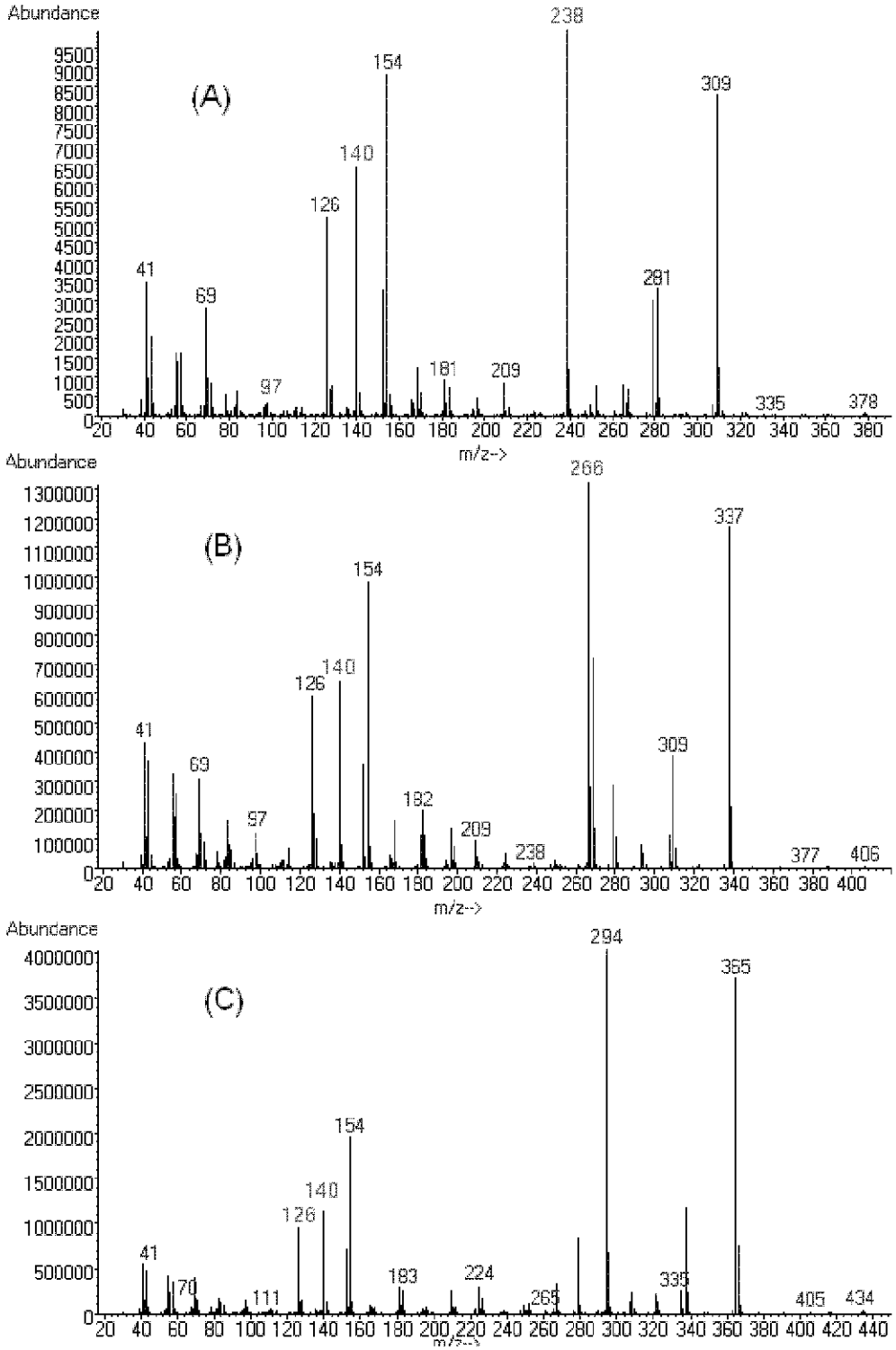


Figure 13. Total ion current GC/MS chromatogram of trifluoroacetylated (TFA) derivatives of Duomeen® CD (top) and Duomeen® TD (bottom) dissolved in tetrahydrofurane. Fused silica capillary column: *HP-5ms*, 30 m, 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 150 °C (1 min hold) at 3 °C min^{-1} to 280 °C (hold 30 min). Split/splitless injector: 250 °C. Helium constant flow of 1 cm^3 min^{-1}, split flow 20 cm^3 min^{-1}. Peak identification: (a) 12.63 min – 1-aminododecane-TFA; (b) 17.77 min – 1-aminotetradecane-TFA; (A) 17.87 min – *N*-1-octyl-1,3-propanediamine-di-TFA; (c) 23.06 min – 1-aminohexadecane-TFA; (B) 23.10 min – *N*-1-decyl-1,3-propanediamine-di-TFA; (d) 28.28 min – 1-aminooctadecane-TFA; (C) 28.66 min – *N*-1-dodecyl-1,3-propanediamine-di-TFA; (D) 33.23 min – *N*-1-tetradecyl-1,3-propanediamine-di-TFA; (E) 37.67 min – *N*-1-hexadecyl-1,3-propanediamine-di-TFA; (F) 39.77 min – *N*-1-heptadecyl-1,3-propanediamine-di-TFA; (G) 41.43 min – *N*-1-octadecenyl-1,3-propanediamine-di-TFA; (H) 42.10 min – *N*-1-octadecyl-1,3-propanediamine-di-TFA.

The mass spectra formed by the electron-impact ionization (EI) of the di-(trifluoroacetylated) *N*-alkyl-1,3-propanediamines (C_8 – C_{18}) identified in Duomeen® CD and Duomeen® TD are presented in Figure 14.


Abundance
(A)
238
154
309
140
126
41
69
281
181
209
97
335
378
m/z-->
Abundance
(B)
266
337
154
140
126
41
69
309
182
209
97
238
377
406
m/z-->
Abundance
(C)
294
365
154
140
126
41
70
111
183
224
265
335
405
434

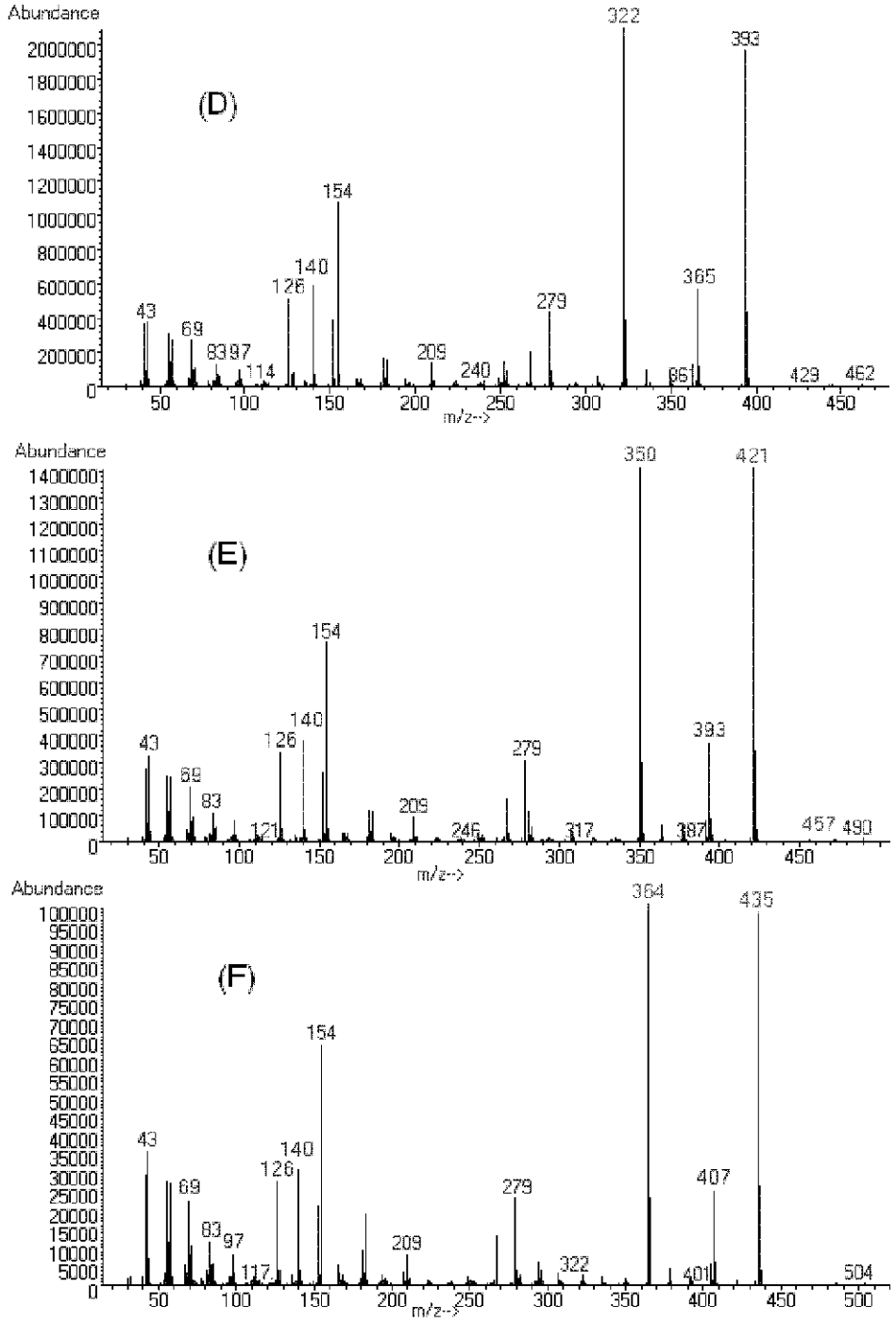


Figure 14. Electron impact ionization (EI) mass spectra of di-(trifluoroacetylated) (di-TFA) derivatives of *N*-alkyl-1,3-propanediamines in Duomeen® CD and Duomeen® TD. For mass spectra identification and proposed chemical structure, see Table 2.

The weak signals for molecular ions $[M]^{+\bullet}$ at *m/z* 378, 406, 434, 462, 490, 504, 516 and 518 in the mass spectra (Figure 14 A–H) corresponds to *N*-1-octyl-1,3-propanediamine-di-TFA, *N*-1-decyl-1,3-propanediamine-di-TFA, *N*-1-dodecyl-1,3-propanediamine-di-TFA, *N*-1-tetradecyl-1,3-propanediamine-di-TFA, *N*-1-hexadecyl-1,3-propanediamine-di-TFA, *N*-1-heptadecyl-1,3-propanediamine-di-TFA, *N*-1-octadecenyl-1,3-propanediamine-di-TFA and *N*-1-octadecyl-1,3-propanediamine-di-TFA, respectively. The characteristic fragments at *m/z* 309, 337, 365, 393, 421, 435, 447 and 449 in Figure 14 are formed by loss of the CF_3-radical from the molecules (equation 6).

$$[\text{R-N(COCF}_3\text{)-(CH}_2\text{)}_3\text{-NH-C(O)CF}_3]^{+\bullet} \rightarrow \underset{[M-69]^+}{[\text{R-N(COCF}_3\text{)-(CH}_2\text{)}_3\text{-NH-C(O)}]^+} + {}^{\bullet}CF_3 \quad (6)$$

where R = C_8H_{17} – $C_{18}H_{37}$.

The peaks at *m/z* 281, 309, 337, 365, 393, 407, 419 and 421 are due to the suitable $[M - CF_3C(O)]^+$ ions of *N*-1-octyl-1,3-propanediamine-di-TFA, *N*-1-decyl-1,3-propanediamine-di-TFA, *N*-1-dodecyl-1,3-propanediamine-di-TFA, *N*-1-tetradecyl-1,3-propanediamine-di-TFA, *N*-1-hexadecyl-1,3-propanediamine-di-TFA, *N*-1-heptadecyl-1,3-propanediamine-di-TFA, *N*-1-octadecenyl-1,3-propanediamine-di-TFA and *N*-1-octadecyl-1,3-propanediamine-di-TFA, respectively. The peak at *m/z* 69 represents the $[CF_3]^+$ ion and the peak at *m/z* 97 corresponds to the $[CF_3C(O)]^+$ ion.

As can be seen from Figure 14 (A–H), each mass spectrum exhibits a series of characteristic fragments at *m/z* 126, 140 and 154. They could be explained by the alkyl cleavage of the *N*-1-alkyl-1,3-propanediamine-di-TFA derivatives with a ring formation reaction producing the ions $[(H_2C)_nN(H)C(O)CF_3]^+$ (n = 1 – 3) (Figure 15). The peak in the mass spectra in Figure 14 (A–H) at *m/z* 154 is due to the $[CF_3C(O)N(H)CH_2CH_2CH_2]^+$ ion. The proposed EI-MS fragmentation pattern for the investigated *N*-1-alkyl-1,3-propanediamines-di-TFA derivatives and the structures of other significant peaks are shown in Figure 15 and in Table 2 [5, 7].

Figure 16 shows the mass spectra obtained by the negative chemical ionization (NCI) of the di-(trifluoroacetylated) *N*-alkyl-1,3-propanediamines (C_8 – C_{18}) identified in Duomeen® CD and Duomeen® TD. The weak signals for molecular ions at *m/z* 378, 406, 434, 462, 490, 504, 516, 518, the quasi-molecular ions $[M - 1]^-$ at *m/z* 377, 405, 433, 461, 489, 503, 515, 517, as well as the fragments $[M - 1 - F]^-$ at *m/z* 358, 386, 414, 442, 470, 484, 496 and 498 in Figure 16 (A–H) corresponds to *N*-1-octyl-1,3-propanediamine-di-TFA, *N*-1-decyl-1,3-propanediamine-di-TFA, *N*-1-dodecyl-1,3-propanediamine-di-TFA, *N*-1-tetradecyl-1,3-propanediamine-di-TFA, *N*-1-hexadecyl-1,3-propanediamine-di-TFA, *N*-1-heptadecyl-1,3-propanediamine-di-TFA, *N*-1-octadecenyl-1,3-propanediamine-di-TFA and *N*-1-octadecyl-1,3-propanediamine-di-TFA, respectively.

The characteristic fragments at *m/z* 125 and 138 are formed through the α- and β-cleavage mechanism of the quasi-molecular ions $[M - 1]^-$ of *N*-1-alkyl-1,3-propanediamines-di-TFA. The proposed NCI-MS fragmentation pattern for the investigated substances and the structures of the significant peaks are shown in Figure 17 and in Table 2 [7].

Table 2. Identification of di-(trifluoroacetylated) (di-TFA) derivatives of *N*-alkyl-1,3-propanediamines in Duomeen® CD and Duomeen® TD (Figures 14 and 16)

Mass spectrum	Significant fragments (*m/z*)		Chemical structure
	EI	NCI	
A	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2]^+$ (126); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (238); $[M - CF_3C(O)]^{+\cdot}$ (281); $[M - CF_3]^+$ (309); $[M]^{+\cdot}$ (378);	$[M - 1 - C_8H_{17}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_8H_{17}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2CH_2]^-$ (224); $[M - 1 - F]^-$ (358); $[M - F]^-$ (359); $[M - 1]^-$ (377); $[M]^-$ (378);	*N*-1-Octyl-1,3-propanediamine-di-TFA
B	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2]^+$ (126); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (266); $[M - CF_3C(O)]^{+\cdot}$ (309); $[M - CF_3]^+$ (337); $[M]^{+\cdot}$ (406);	$[M - 1 - C_{10}H_{21}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_{10}H_{21}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2CH_2]^-$ (252); $[M - 1 - F]^-$ (386); $[M - F]^-$ (387); $[M - 1]^-$ (405); $[M]^-$ (406);	*N*-1-Decyl-1,3-propanediamine-di-TFA
C	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (294); $[M - CF_3C(O)]^{+\cdot}$ (337); $[M - CF_3]^+$ (365); $[M]^{+\cdot}$ (434);	$[M - 1 - C_{12}H_{25}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_{12}H_{25}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2CH_2]^-$ (280); $[M - 1 - F]^-$ (414); $[M - F]^-$ (415); $[M - 1]^-$ (433); $[M]^-$ (434);	*N*-1-Dodecyl-1,3-propanediamine-di-TFA
D	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (322); $[M - CF_3C(O)]^{+\cdot}$ (365); $[M - CF_3]^+$ (393); $[M]^{+\cdot}$ (462);	$[M - 1 - C_{14}H_{29}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_{14}H_{29}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2CH_2]^-$ (308); $[M - 1 - F]^-$ (442); $[M - F]^-$ (443); $[M - 1]^-$ (461); $[M]^-$ (462);	*N*-1-Tetradecyl-1,3-propanediamine-di-TFA

Table 2. (Continued)

Mass spectrum	Significant fragments (*m/z*)		Chemical structure
	EI	NCI	
E	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (350); $[M - CF_3C(O)]^{+\cdot}$ (393); $[M - CF_3]^+$ (421); $[M]^{+\cdot}$ (490);	$[M - 1 - C_{16}H_{33}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_{16}H_{33}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2CH_2]^-$ (336); $[M - 1 - F]^-$ (470); $[M - F]^-$ (471); $[M - 1]^-$ (489); $[M]^-$ (490);	*N*-1-Hexadecyl-1,3-propanediamine-di-TFA
F	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (364); $[M - CF_3C(O)]^{+\cdot}$ (407); $[M - CF_3]^+$ (435); $[M]^{+\cdot}$ (504);	$[M - 1 - C_{17}H_{35}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_{17}H_{35}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2CH_2]^-$ (350); $[M - 1 - F]^-$ (484); $[M - F]^-$ (485); $[M - 1]^-$ (503); $[M]^-$ (504);	*N*-1-Heptadecyl-1,3-propanediamine-di-TFA
G	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (376); $[M - CF_3C(O)]^{+\cdot}$ (419); $[M - CF_3]^+$ (447); $[M]^{+\cdot}$ (516);	$[M - 1 - C_{18}H_{35}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_{18}H_{35}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2\ CH_2]^-$ (362); $[M - 1 - F]^-$ (496); $[M - F]^-$ (497); $[M - 1]^-$ (515); $[M]^-$ (516);	*N*-1-Octadecenyl-1,3-propanediamine-di-TFA
H	$[CONH]^+$ (43); $[CF_3]^+$ (69); $[CF_3C(O)]^+$ (97); $[CF_3C(O)NHCH_2CH_2]^+$ (140); $[CF_3C(O)NHCH_2CH_2CH_2]^+$ (154); $[M - CF_3C(O)NHCH_2CH_2]^{+\cdot}$ (378); $[M - CF_3C(O)]^{+\cdot}$ (421); $[M - CF_3]^+$ (449); $[M]^{+\cdot}$ (518);	$[M - 1 - C_{18}H_{37}N(CF_3CO)CH_2CH_2]^-$ (125); $[M - 2 - C_{18}H_{37}N(CF_3CO)CH_2]^-$ (138); $[M - CF_3C(O)NHCH_2CH_2CH_2]^-$ (364); $[M - 1 - F]^-$ (498); $[M - F]^-$ (499); $[M - 1]^-$ (517); $[M]^-$ (518);	*N*-1-Octadecyl-1,3-propanediamine-di-TFA

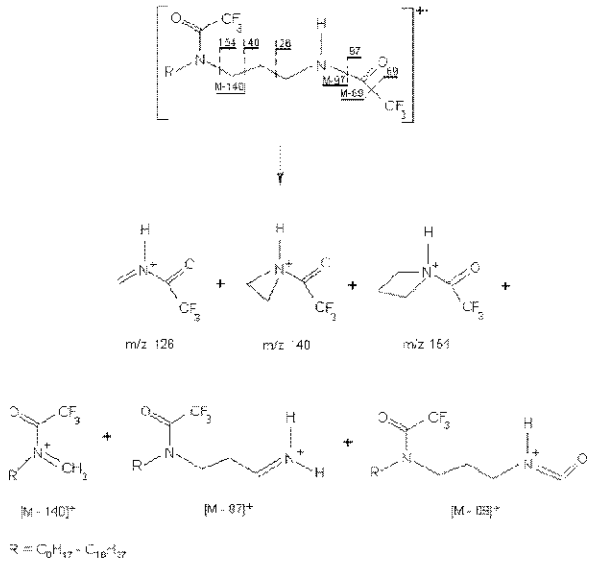


Figure 15. Proposed EI-MS fragmentation pattern for di-(trifluoroacetylated) derivatives of *N*-alkyl-1,3-propanediamines. For mass spectra, see Figure 14.

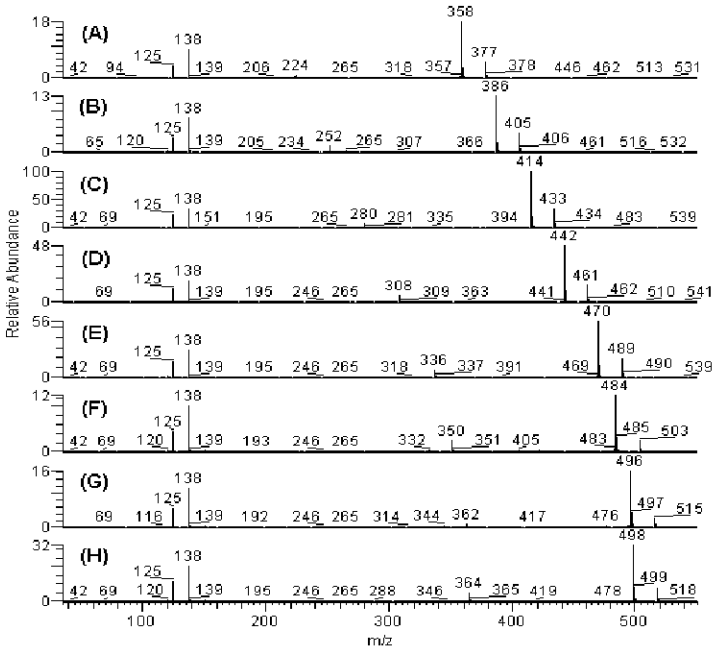


Figure 16. Negative chemical ionization (NCI) mass spectra of di-(trifluoroacetylated) (di-TFA) derivatives of *N*-alkyl-1,3-propanediamines in Duomeen® CD and Duomeen® TD. For mass spectra identification and proposed chemical structure, see Table 2.

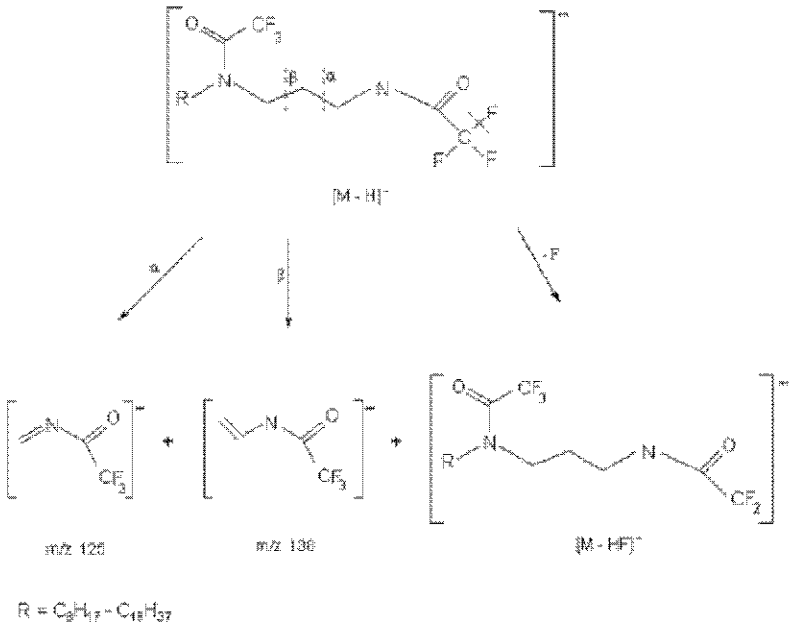


Figure 17. Proposed NCI-MS fragmentation pattern for di-(trifluoroacetylated) derivatives of *N*-alkyl-1,3-propanediamines. For mass spectra, see Figure 16.

Quantitative Determination of Primene JM-T™ in Water Samples from the Power Plant

The linearity of both FID and NPD for the quantitative determination of Primene JM-T™ in boiler water, condensate and superheated steam samples from the power plant was evaluated by consecutive injecting of standard solutions (see Experimental). Each standard solution was injected in triplicate and the mean value of the total peak area ratio Primene JM-T™-TFA/I.S. was taken for construction of the calibration line. The total peak area of Primene JM-T™-TFA means the sum of all peaks area of trifluoroacetylated *tert*-octadecylamines in the sample. The calibration graphs obtained in Figure 18 [3] show the relationship between the obtained total peak area ratio Primene JM-T™-TFA/I.S. and the concentration of Primene JM-T™-TFA in the standard solutions for FID and NPD, respectively. The quantity of Primene JM-T™ in boiler water, condensate and superheated steam samples from the power plant was calculated from results of chromatographic analyses and results of detectors calibration using the equation 7:

$$C_{\text{i sample}} = \frac{(A'_{\text{sample}} - b) \cdot 100\%}{a \cdot f \cdot R} \qquad (7)$$

where $C_{\text{i sample}}$ is the concentration (mg L^{-1}) of Primene JM-T™ in the sample, A'_{sample} is the total peak area ratio Primene JM-T™-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™ from the water sample. The total peak area ratio Primene JM-T™- TFA/I.S. in the sample (A'_{sample}) was calculated from the equation 8:

$$A'_{sample} = \frac{A_{i\ sample} \cdot m_{I.S.\ sample}}{A_{I.S.\ sample} \cdot m_{I.S.\ cal}} \qquad (8)$$

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

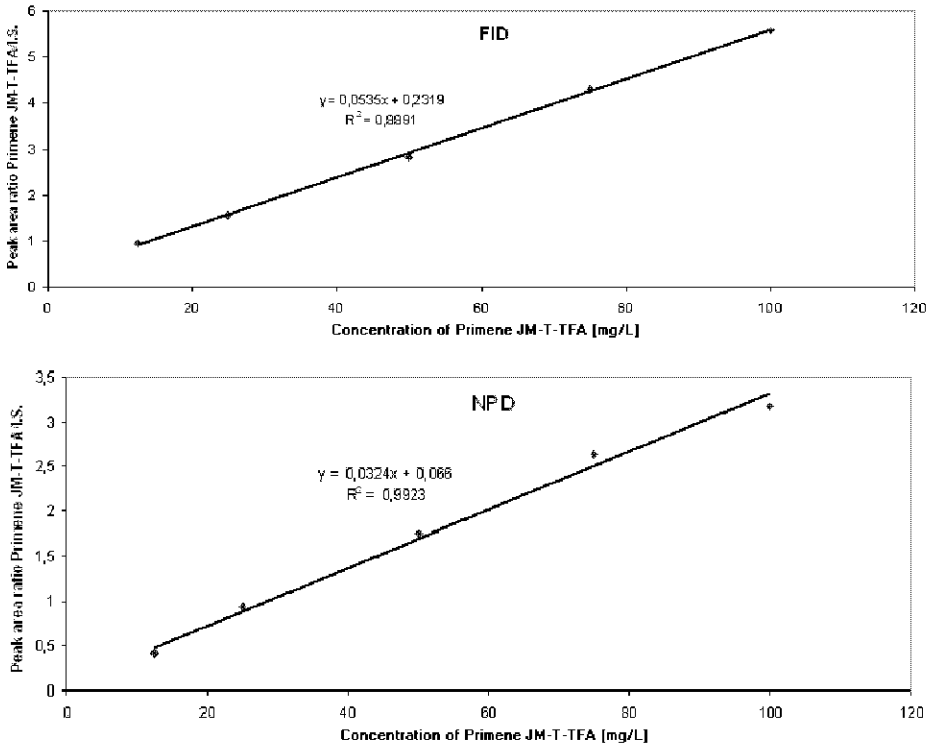


Figure 18. Total peak area ratio Primene JM-T™-TFA/I.S. *vs.* concentration of Primene JM-T™-TFA in the standard solutions for FID (top) and NPD (bottom).

Figure 19 shows the SPE-GC/FID chromatograms of the investigated water samples from the Power Plant Białystok (Poland). The concentrations of Primene JM-T™ determined as the sum of *tert*-octadecylamines in boiler water, condensate and superheated steam samples from the same power plant were 89 μg L^{-1} (n = 5, RSD = 7.8 %), 37 μg L^{-1} (n = 5, RSD = 2.3 %) and 45 μg L^{-1} (n = 5, RSD = 5.4 %), respectively.

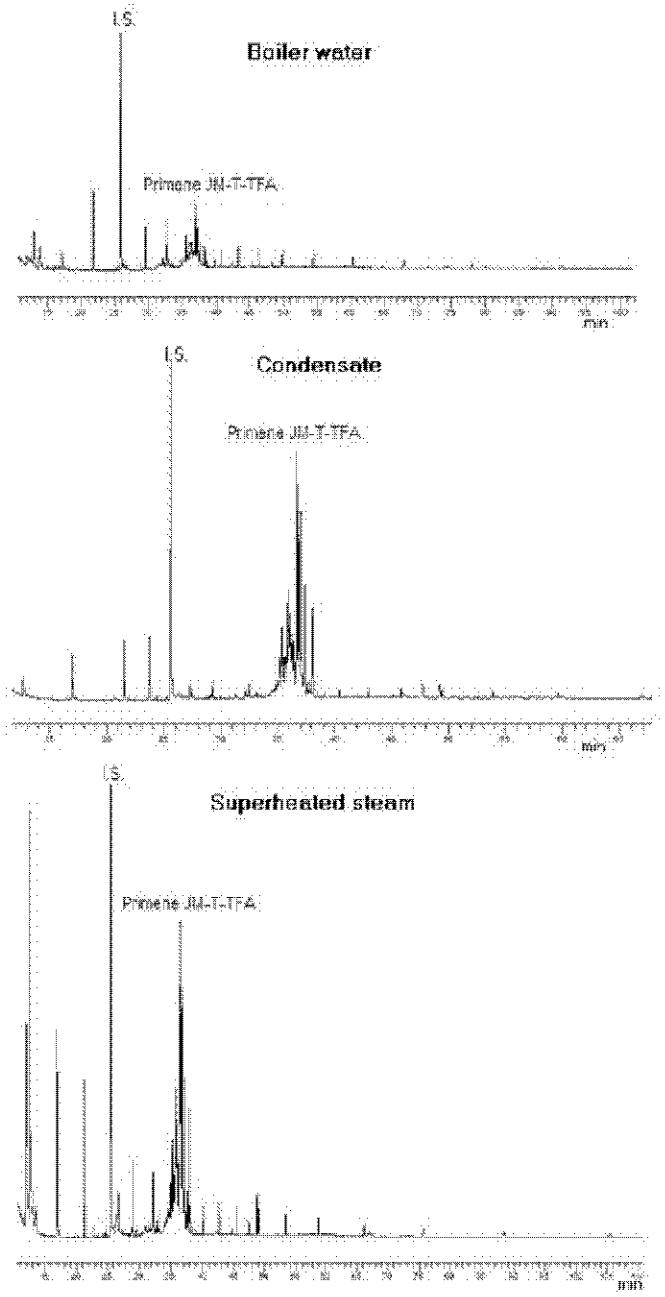


Figure 19. SPE-GC/FID chromatograms of boiler water (top), condensate (middle) and superheated steam (bottom) samples from the Power Plant Białystok (Poland). Fused silica capillary column: *DB-5ms*, 60 m x 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 60 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 80 min). Split/splitless injector: 290 °C. Helium constant pressure 140 kPa, split flow 20 cm^3 min^{-1}. FID: 320 °C. Peak identification: t_R = 25.46 min: dicyclohexylamine (internal standard, I.S.); t_R = 36.52 min: 8-methyl-8-heptadecaneamine-TFA; t_R = 36.58 min: 7-methyl-7-heptadecaneamine-TFA; t_R = 36.70 min: 6-methyl-6-hetadecaneamine-TFA; t_R = 36.87 min: 5-methyl-5-heptadecaneamine-TFA; t_R = 37.22 min: 4-methyl-4-heptadecaneamine-TFA; t_R = 37.95 min: 3-methyl-3-heptadecaneamine-TFA; t_R = 38.05 min: 2-methyl-2-heptadecaneamine-TFA .

CONCLUSION

Gas chromatography with simultaneous flame-ionization detection (FID) and a nitrogen-phosphorus detection (NPD) as well as gas chromatography-mass spectrometry (GC/MS) with electron impact ionization (EI) and chemical ionization (PCI and/or NCI) were successfully used for separation and identification of commercially available long-chain primary alkyl amines and alkyl diamines. The investigated compounds were used as corrosion inhibiting and antifouling agents 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 Primene JM-T™ alkyl amines in boiler water, condensate and superheated steam samples from the power plant.

ACKNOWLEDGMENTS

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