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Identification and Application of Corrosion Inhibiting Long-Chain Primary Alkyl Amines in Water Treatment in the Power Industry

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Additional information is available at the end of the chapter

1. Introduction

Heated boilers are an essential element of industrial processes. They need to be reliable and kept in good working order. With skyrocketing fuel and energy costs, maintaining the reliability and consistent performance of a boiler while minimizing energy costs, is challenging for any industrial works. Since boiler systems are constructed primarily of carbon steel and the medium for heat transfer is water, the potential threat for corrosion, scale forming and bio-fouling is great. The build up of corrosion can result in a forced shutdown of the boiler and the whole industrial process [1].

Certain chemical and thermal conditions favor the occurrence of corrosion processes on the surfaces of heated boilers. This phenomenon is a result of chemical reactions taking place in non-homogenous steam-water environment, which have often a local nature and, additionally, are difficult to determine in qualitative analysis of working medium [2]. In high pressure boiler drums, where feed water is even one hundred times more concentrated (even more in regions where steam bubbles are generated) it is difficult to avoid scaling and corrosion of boiler's construction walls. Even a relatively slight decrease in boilers efficiency caused by scale leads to increase in fuel consumption up to hundreds of tons annually [2]. Finding ways to operate a large cooling water system economically while maximizing heat transfer is a complex and challenging task.

One of the effective ways to improve installation economics and reliability is protective water treatment with chemical formulations containing corrosion inhibitors [2]. In the past, the efficient protective treatments of carbon steels were based on inorganic inhibitors like ammo-

nia, nitrites, phosphates or chromates. Today, their use is restricted due to their high toxicity and environmental impact. The most common protective water treatment methods base on the use of neutralizing amines. These chemicals, such as morpholine, cyclohexylamine and *N,N*-diethylhydroxylamine (DEHA) neutralize the carbonic acid (formed in the reaction of carbon dioxide with water) and increase the pH of the condensate [3].

In the first half of the 20th century the aliphatic monoamines [$CH_3(CH_2)_nNH_2$, $n = 10 \div 20$] and alkyl polyamines [$R-(NH-CH_2-CH_2-CH_2-)_nNH_2$, $n = 1 \div 5$] drew researchers' attention due to their exceptional ability to form thin adhesive films, usually monomolecular, which strongly bond to the metal surface. In this layer, referred to as an amine film, amine groups ($-NH_2$) are bonded to a metal surface, while long hydrophobic hydrocarbon chains are oriented in opposite direction, which works as a barrier protecting the metal surface against gaseous molecules (O_2, CO_2) as well as ionic pollutants (*e.g.* Cl^-, SO_4^{2-}) [2].

Despite the fact that use of organic chemical agents in anti-corrosion protection is not recommended by several international regulations, many film-forming amines (FFA) have been used in the power industry and in heat engineering [2-4]. Just like in classical treatment concepts, treatment with FFA must be carefully monitored in order to ensure successful treatment and a high degree of operational safety. Sampling points are the boiler feed-water, the boiler water and the condensate. The condensate should have a slightly alkaline pH and it should be possible to detect an excess of free FFA [4].

At the end of 1980 the Instytut Ciężkiej Syntezy Organicznej "Blachownia" (Institute of Heavy Organic Synthesis "Blachownia") (Kędzierzyn-Koźle, Poland) along with ZPBE ENERGOPOMIAR Ltd. (Gliwice, Poland) and P.U.B. "Ekochem" Ltd. (Gliwice, Poland) worked out a group of multifunctional amine formulations named *Kotamina* [5-7]. These formulations contain an appropriately composed mixture of alkyl amines (main component) with different partition coefficients, which enables control of corrosion kinetics within a whole system through dosing of these formulations into condensate, feed water or make-up water. The presence of alkalizing amines in the formulation helps in keeping constant pH in a desired range, whereas alkyl amines, both render the water alkaline and limit the corrosive impact of ionic and gaseous impurities by formation of monomolecular protective films. The alkyl amines were chosen on the basis of results obtained during investigation of their influence on the adsorption on metal surfaces. The utility properties of these formulations as well as experience related to their application in Polish power industry for over twenty years were presented in several papers [5-7].

2. Thermostable alkyl amines as a base for anti-corrosive and anti-scaling formulations

Alkyl amines used at present in correction formulations exhibit limited stability toward higher temperatures and their decomposition starts at temperatures slightly above 300 °C. One disadvantage of alkyl amine formulations application in the field was the high concentration of ammonia in the condensate and in the steam caused by decomposition of amines of higher

molecular weight. Utilization of thermostable alkyl amines in water treatment technology, whose decomposition is above 500 °C, causes decrease in ammonia levels and improves anti-corrosive protection of the brass elements [2].

Achieving further improvement in correction technology of steam-water systems, additional investigations with usage of thermostable, branched long-chain alkyl amines (as a base for correction formulations) were developed. The research on the application of thermostable alkyl amines in water treatment was performed within the framework of the international project EUREKA E!2426 BOILTREAT "New technology of boiler water treatment" with partners from research institutes, industry and academia from Poland, Lithuania, Romania, France and Germany [8]. Thus, a new anticorrosion agent called *Kotamina Plus* was formulated, which contains branched long-chain primary alkyl amines of the Primene JM-T™ type [9-11].

Others multifunctional anti-corrosive and anti-scaling formulations based on alkyl amines were described in several publications or patents [12-18].

3. Identification and determination of corrosion inhibiting long-chain primary alkyl amines of the Primene JM-T™ type by gas chromatography (GC) and gas chromatography - mass spectrometry (GC/MS)

3.1. Chemicals and samples

Alkyl amines Primene JM-T™ obtained from Rohm and Haas France S.A.S. (Valbonne, France), dicyclohexylamine for synthesis from Merck-Schuchardt (Hohenbrunn, Germany), *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% dimethydi-chlorosilane (DMDCS) in toluene (Sylon CT) for glass silylation from Supelco (Bellefonte, PA, U.S.A.) and deionized 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.

To prevent adsorption of alkyl amines on the glass surface, spiked water samples of 10 mg 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).

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 in 10 cm³ silylated volumetric flask.

For solid phase extraction (SPE) of organic compounds from water samples LiChrolut RP-18 E (octadecyl, endcapped, 500 mg/3 cm³) cartridges supplied by Merck were used.

3.2. Derivatization procedure

Amines are generally known to be very difficult to analyze by gas chromatography (GC) due to their basic character [19, 20]. 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. 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. Derivatized analyte offer a greater response to the chromatographic detection system than the parent compounds. 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 trifluoro-acetic acid anhydride (TFAA) as derivatization method for alkyl amines. A benefit of acylation is the formation of fragmentation-directing derivatives for GC/MS analysis [19].

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 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 or GC/MS.

3.3. Solid-phase extraction (SPE) of water samples from the power plant

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 thirty years, SPE has become the most powerful technique available for rapid and selective sample preparation prior to analytical chromatography.

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) and extracted by solid-phase extraction from a 1 L PP volumetric flask (Kartell). For conditioning the SPE LiChrolut® RP-18 E cartridge packing, the tube was rinsed with 6 cm³ methanol followed with 6 cm³ deionised water. After the conditioning step 1–2 L of the investigated water sample were percolated at a flow rate of 5 cm³ min⁻¹ through the SPE tube. After washing the tube with 5 cm³ of deionised water, the adsorbed organic compounds were eluted in a mixture of 5 cm³ *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 in 3.2. The resulting product was dissolved in 1 cm³ of the internal standard solution, containing 10 - 12 mg L⁻¹ of dicyclohexylamine in *n*-hexane and analyzed by GC-FID.

3.4. Instrumentation

Gas chromatographic (GC) analyses were performed with an *Autosystem* or an *Clarus 500* gas chromatograph from PerkinElmer Instruments (Norwalk, CT, U.S.A.), both equipped with a split/splitless injector at 290 °C and a flame-ionization detector (FID) 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 and the split flow was 20 cm³ 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 J&W Scientific (Folsom, CA, U.S.A.). The oven temperature was programmed from 60 °C (1 min hold) at 6 °C min⁻¹ to 280 °C (hold 50 min). Chromatographic data were processed with *TotalChrom Workstation* software, version 6.3. (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 Ther-moQuest *Xcalibur* data system, the *NIST 05* mass spectra library, and a *CombiPAL* autosampler (CTC Analytics AG, Zwingen, Switzerland). The fused silica capillary columns, 60 m long, 0.25 mm I. D. with *DB-5ms* (J&W) or *Elite-5ms* (PerkinElmer Instruments) stationary phases, film thickness 0.25 μm were used. The temperature of the columns 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 cm³ 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 cm³ 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 150 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 also 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) was used as a carrier gas. Constant flow of helium of 1.0 cm³ min⁻¹ was used during the whole analysis. The temperature of the split/splitless injector was 250 °C and the split flow was 10 cm³ 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 35-750 u.

3.5. Results and discussion

3.5.1. Structure elucidation of long-chain primary alkyl amines of the Primene JM-T™ type

The general reaction for acylation of the investigated long-chain primary alkyl amines with trifluoroacetic anhydride (TFAA) is shown in equation (1):

$$(R_1)(R_2)(R_3)C\text{-}NH_2 + (CF_3CO)_2O \longrightarrow (R_1)(R_2)(R_3)C\text{-}NH\text{-}C(O)CF_3 + CF_3COOH \qquad (1)$$
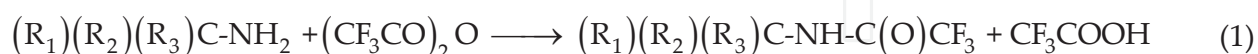
Figure 1 shows a typical total ion current GC/MS chromatogram of trifluoroacetylated (TFA) derivative of Primene JM-T™ dissolved in *n*-hexane. The obtained electron impact (EI) mass spectra of the separated compounds from Primene JM-T™-TFA as well as the mass spectra recorded in the negative chemical ionization mode (NCI) and in the positive ionization (PCI) mode, respectively are presented in our previous publications [20-23].

Table 1 summarized the significant *m/z* fragments in the recorded mass spectra of the investigated TFA derivative of Primene JM-T™.
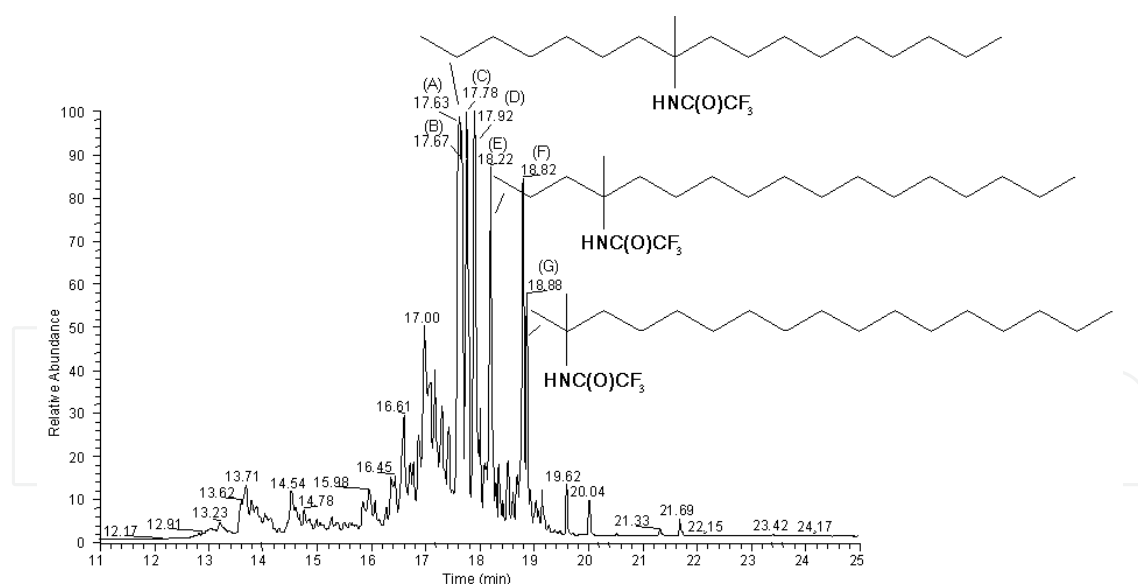

Figure 1. Total ion current GC/MS chromatogram of trifluoroacetylated (TFA) derivative of Primene JM-T™ dissolved in *n*-hexane. Fused silica capillary column: *DB-5ms*, 60 m x 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 150 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 30 min). Split/splitless injector: 250 °C. Helium constant flow 1 cm³ min^{-1}, split flow 100 cm³ 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 [23]. Publishing with licence number 3185340683087 from Elsevier.

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); $[M - C_9H_{19}]^{+\cdot}$ (238); $[M - C_8H_{17}]^{+\cdot}$ (252); $[M - C_7H_{15}]^{+\cdot}$ (266);	$[M - 1 - C_9H_{19}]^{-\cdot}$ (237); $[M - 1 - C_8H_{17}]^{-\cdot}$ (251); $[M - 1 - C_7H_{15}]^{-}$ (265); $[M - 1]^{-\cdot}$ (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); $[M - C_{10}H_{21}]^{+\cdot}$ (224); $[M - C_6H_{13}]^{+\cdot}$ (280);	$[M - 1 - C_{10}H_{21}]^{-\cdot}$ (223); $[M - 1 - C_6H_{13}]^{-\cdot}$ (279); $[M - 1]^{-\cdot}$ (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); $[M - C_{11}H_{23}]^{+\cdot}$ (210); $[M - C_5H_{11}]^{+\cdot}$ (294);	$[M - 1 - C_{11}H_{23}]^{-\cdot}$ (209); $[M - 1 - C_5H_{11}]^{-\cdot}$ (293); $[M - 1]^{-\cdot}$ (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); $[M - C_{12}H_{25}]^{+\cdot}$ (196); $[M - C_4H_9]^{+\cdot}$ (308);	$[M - 1 - C_{12}H_{25}]^{-\cdot}$ (195); $[M - 1 - C_4H_9]^{-\cdot}$ (307); $[M - 1]^{-\cdot}$ (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); $[M - C_{13}H_{27}]^{+\cdot}$ (182); $[M - C_3H_7]^{+\cdot}$ (322);	$[M - 1 - C_{13}H_{27}]^{-\cdot}$ (181); $[M - 1 - C_3H_7]^{-\cdot}$ (321); $[M - 1]^{-\cdot}$ (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); $[M - C_{14}H_{29}]^{+\cdot}$ (168);	$[M - 1 - C_{14}H_{29}]^{-\cdot}$ (167); $[M - 1 - C_2H_5]^{-\cdot}$ (335); $M - 1]^{-\cdot}$ (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);	3-methyl-3-heptadecaneamine-TFA

Mass spectrum	Significant fragments (m/z)			Chemical structure
	EI	NCI	PCI	
	$[M - C_2H_5]^{+\cdot}$ (336);		$[M + H]^+$ (366);	
G	$[CF_3]^+$ (69);	$[M - 1 - C_{15}H_{31}]^{-\cdot}$	$[M + H - C_{15}H_{32}]^+$ (154);	2-methyl-2-
	$[CF_3C(O)]^+$ (97);	(153);	$[M + H - CF_3C(O)NH_2]^+$ (253);	heptadecaneamine-
	$[CF_3C(O)NHCHCH_3]^+$ (140);	$[M - 1 - CH_3]^{-\cdot}$	$[M + H – CH_4]^+$ (350);	TFA
	$[M - C_{15}H_{31}]^+$ (154);	(349);	$[M - H]^+$ (364);	
	$[M - CH_3]^{+\cdot}$ (350);	$[M - 1]^-$ (364);	$[M + H]^+$ (366);	

Table 1. Significant fragments and identification of trifluoroacetylated (TFA) derivatives of *tert*-octadecylamines in Primene JM-T™ [21, 23]. Publishing with licence number 3185351058212 from Elsevier.

The proposed PCI fragmentation pattern for *N*-(*tert*-octadecyl)-trifluoroacetamides is shown in Figure 2 [22, 23]. The proposed chemical structures of the trifluoroacetylated *tert*-octadecylamines are summarized in Table 1.

3.5.2. Quantitative determination of Primene JM-T™ in water samples from the power plant

Gas chromatography with flame ionization detection (GC-FID) was used for the quantitative determination of Primene JM-T™ in boiler water, condensate and superheated steam samples from the power plant. The linearity of FID for the quantitative determination of Primene JM-T™ was evaluated by consecutive injecting of standard solutions (see 3.1). 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 graph obtained in Figure 3 shows 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. 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 (2):

$$C_{i\ sample} = \left[\left(A'_{sample} - b \right) / a \cdot f \cdot R \right] \cdot 100\% \tag{2}$$

where $C_{i\ sample}$ 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 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 (3):

$$A'_{sample} = \left(A_{i\,sample} \cdot m_{I.S.\,sample} \right) / \left(A_{I.S.\,sample} \cdot m_{I.S.\,cal} \right) \tag{3}$$

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 4 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.

4. Corrosion studies

Corrosion studies were performed at the Lithuanian Energy Institute in Kaunas [24]. The results obtained in experiments performed within a temperature range between 20 and 500 ^{0}C, show that the anticorrosion protection increases as temperature becomes higher [2]. In the presence of the new formulation *Kotamina Plus*, the corrosion rate was seven times lower than for non-inhibited water at 90 ^{0}C, and two and half times lower than that in water inhibited with sodium hexametaphosphate (Na PO$_3$)$_6$. It is important to note that *Kotamina Plus* appears to be over 30% more efficient than *Kotamina.* The corrosion rate at 500 ^{0}C for a boilers' steel equals 0.34 µm/year (see Figure 5) [24].

5. Industrial applications

Alkyl amines with branched structure are more thermally stable than linear alkyl amines, and exhibit better adsorption and effectiveness in surface shielding protection [2]. One of the basic features of high molecular mass alkyl amines as components of correction formulations is their influence on improvement of heat exchange in boiler and in turbine condensers. In order to determine this influence for *Kotamina Plus* appropriate investigations in the Engineering Department of Polish Academy of Sciences (PAN) were performed. Results of these experiments show that application of *Kotamina Plus* leads to increase of the convective heat transfer coefficient during boiling by 55% and to increase in heat flux by over 120%. Finally, heat flux during condensation is increased by over 120% in comparison to demineralised water [2]. This improves the efficiency of the entire power unit and lowers the temperature of boiler pipes, helping to avoid overheating.
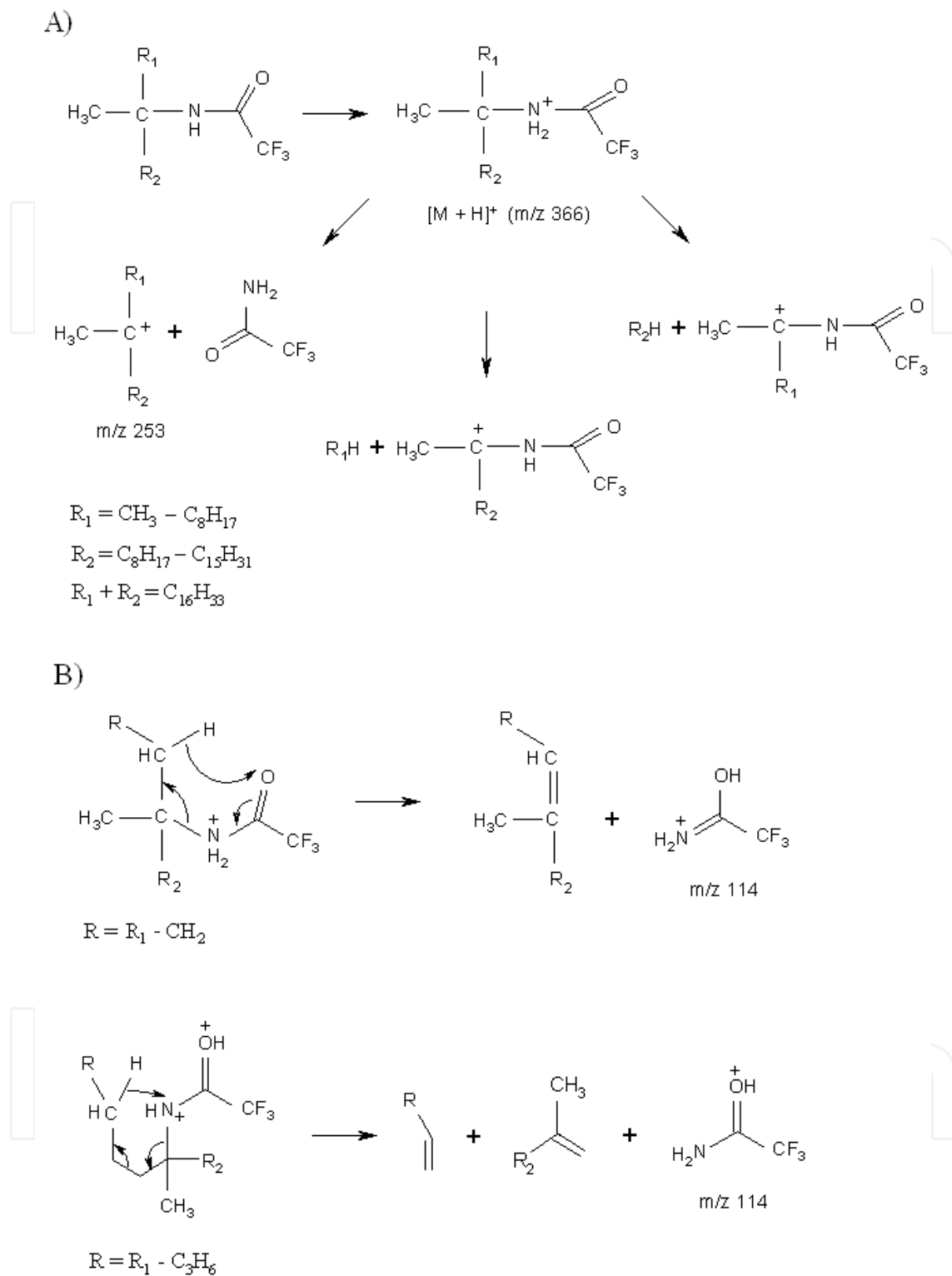
Figure 2. Proposed PCI-MS fragmentation pattern for investigated *N*-(*tert*-octadecyl)-trifluoroacetamides. A) Cleavage mechanism, B) McLafferty rearrangement [22, 23]. Publishing with licence number 3185330243225 from Elsevier.

In the industrial investigations performed in Polish power plants as well as in thermal-electric power plants, *Kotamina Plus* exhibited excellent efficiency in anti-corrosive protec-

tion assuring high purity of circulating medium, and therefore meeting requirements related to boilers exploitation. Experiments performed on a WT 230 boiler's circulating system showed that substitution of *Kotamina* by *Kotamina Plus* results in decrease of iron content by 60% in boiler water, by 30% in saturated and superheated steam, by 25% in condensate and by 40% in make-up water (Figure 6). As a result of *Kotamina Plus* application in WT 650 boiler, the total iron content in particular streams was decreased by over 10% and modification of formulation (*Kotamina Plus/P*) caused further decrease by ca. 30% in boiler water and from 15 to 25% in other streams (Figure 7). The ammonia content was significantly decreased in all streams to 1/3 of non-normalized value but the widely accepted upper limit is 500 $\mu g/dm^3$. This is important for protection against corrosion of brass elements, especially in turbine condensers. Low ammonia concentration positively influences stabilization of pH value in the system and considerable influences mating of boiler and sub-turbine heat exchangers.
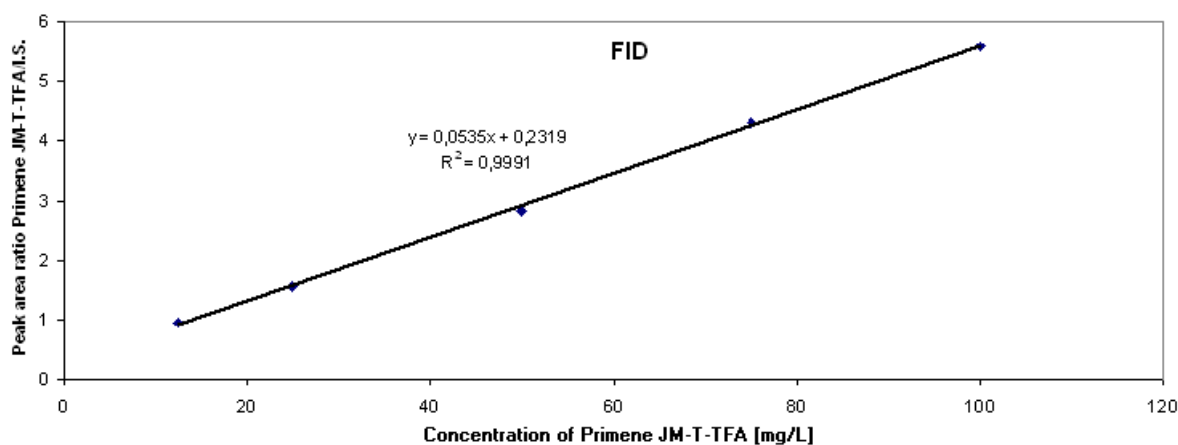

Figure 3. Total peak area ratio Primene JM-T™-TFA/I.S. *vs.* concentration of Primene JM-T™- TFA in the standard solutions for FID [20]. Publishing with licence number 3185340683087 from Elsevier.

Application of alkyl amine formulations instead of phosphate and hydrazine leads to considerable conductivity drop of the boiler water. *Kotamina Plus* introduction, as a result of decreased ammonia concentration, caused further conductivity drop in boiler water as well as in feed water. It allows to lower the desalination of the boiler and to save make-up water as well as energy needed for its heating. Lower ammonia concentration additionally stabilizes the pH value for particular streams. In WT 650 boilers for both blocks (B1 and B2) the pH was raised and for live steam and condensate pH was lowered. This is advantageous because it counteracts the wear of constructional material of a turbine condenser, which possesses brazen piping (Figure 8).
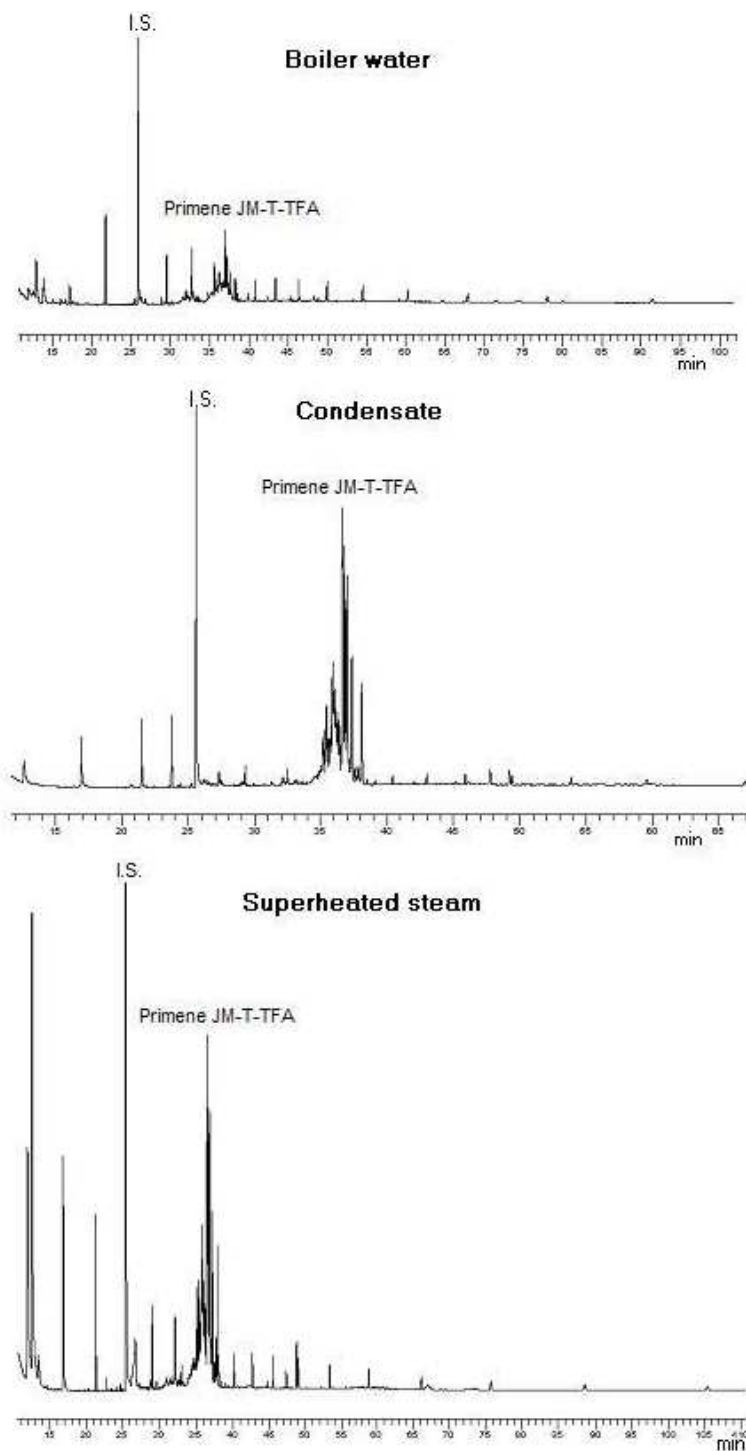
Figure 4. SPE-GC/FID chromatograms of boiler water (top), condensate (middle) and superheated steam (bottom) samples from Power Plant Białystok (Poland) [23]. Fused silica capillary column: *DB-5ms*, 60 m x 0.25 mm I.D., film thickness 0.25 μm. Column temperature programmed from 60 °C (1 min hold) at 6 °C min^{-1} to 280 °C (hold 50 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.
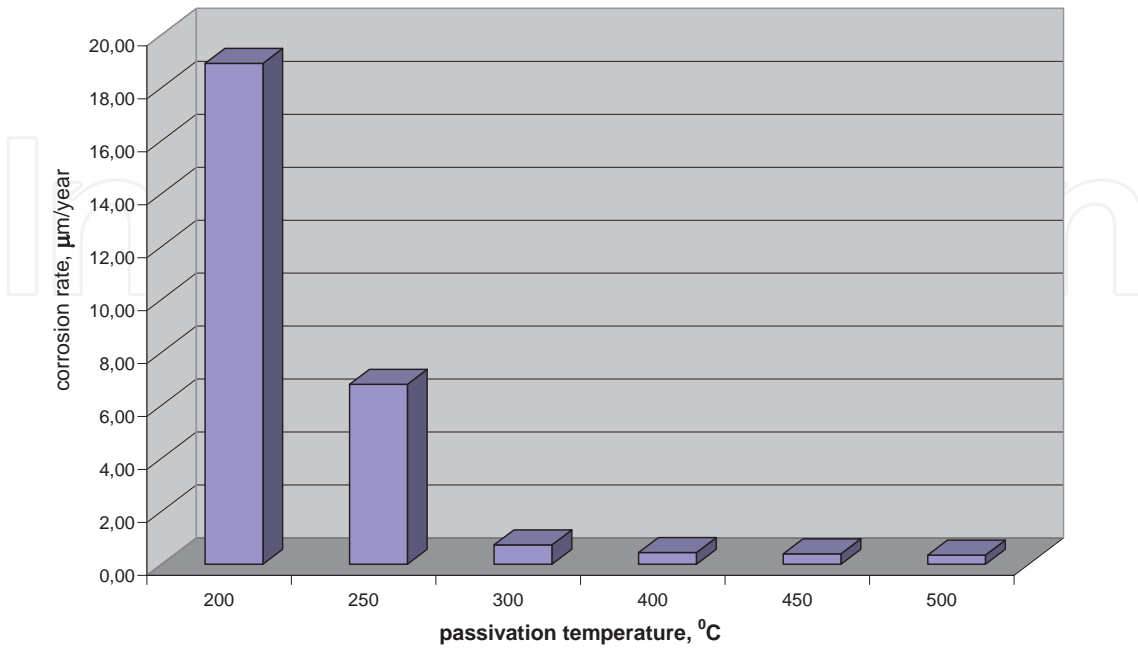
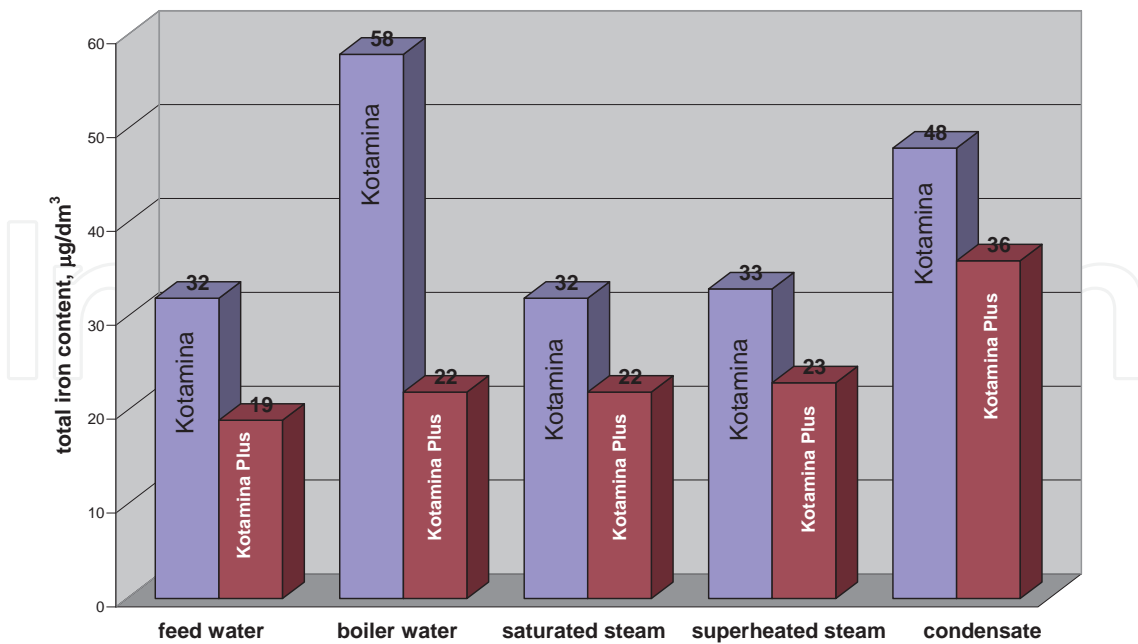**Figure 5.** Dependence of corrosion rate on temperature for boilers' steel [2, 24].

Figure 6. Total iron content in particular streams – WT 230 boiler [2, 24].
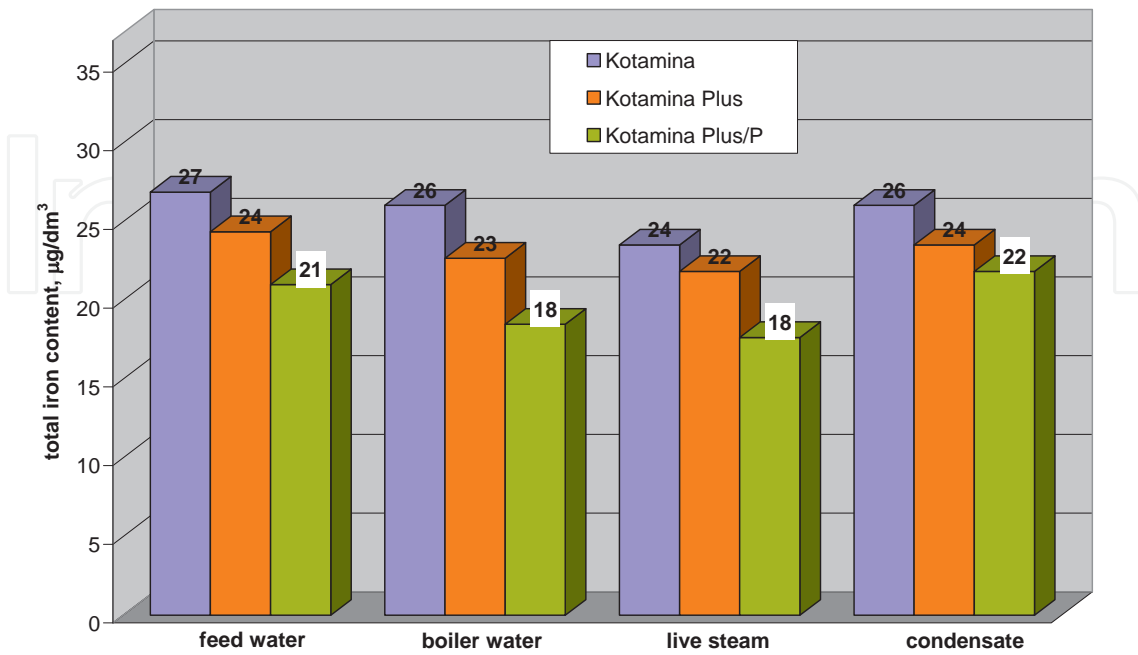
Figure 7. Total iron content in individual streams – average value [2, 24].
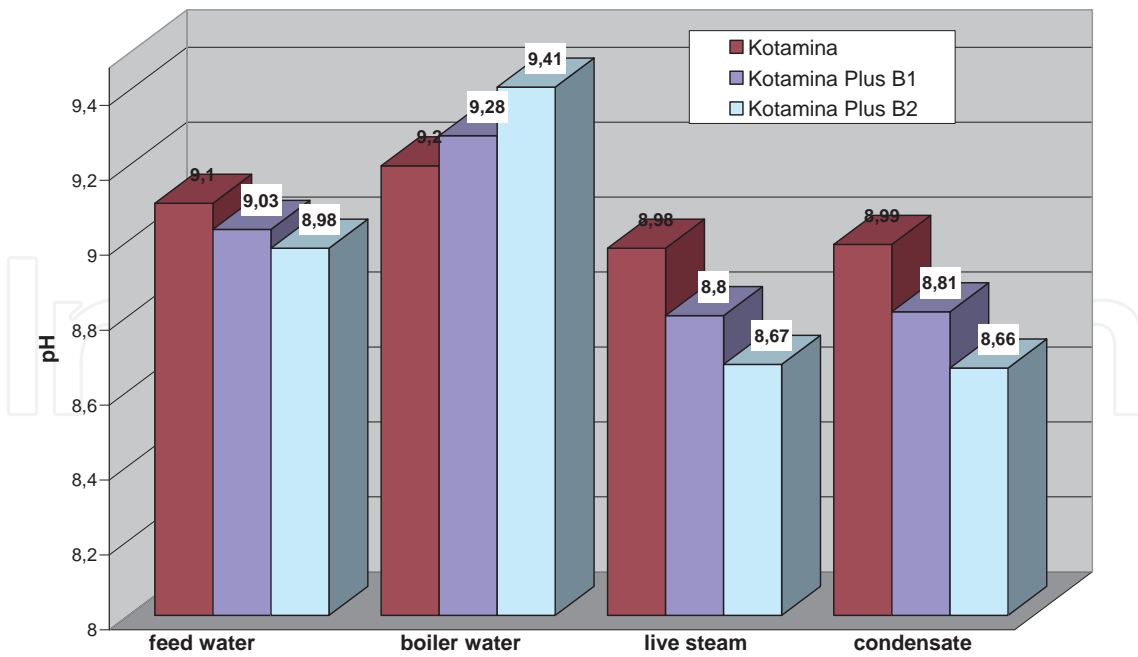

Figure 8. pH values in individual streams – average value [2].

6. Conclusions

Gas chromatography with flame-ionization detection (FID) and gas chromatography-mass spectrometry (GC/MS) with electron impact ionization (EI) and chemical ionization (PCI and NCI) were successfully used for separation and identification of commercially available long-chain primary alkyl amines. 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.

Amine formulations from *Kotamina* group favor formation of protective layers on internal surfaces and keep them free from corrosion and scale. Alkyl amines contained in those formulations both render the environment alkaline and limit the corrosion impact of ionic and gaseous impurities by formation of protective layers. Moreover, alkyl amines limit scaling on heating surfaces of boilers and in turbine, ensuring failure-free operation. Application of alkyl amine formulation enhances heat exchange during boiling and condensation processes. Alkyl amines with branched structure are more thermally stable than linear alkyl amines, exhibit better adsorption and effectiveness of surface shielding. As a result, application of thermostable long-chain branched alkyl amines increases the efficiency of anti-corrosive protection. Moreover, the concentration of ammonia content in water and in steam was also considerably decreased.

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