Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 244 (2005) 155–163

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Direct CIMS for the determination of mixtures of fatty alcohols from octanol to octadecanol

Axel Patrick Ligon [a,∗], Siegmar Gäb [b]

[a] *Institute of Environmental Research (INFU), University of Dortmund, Otto-Hahn-Strasse 6, 44221 Dortmund, Germany*
[b] *Department of Analytical Chemistry, University of Wuppertal, Gauss-Strasse 20, 42097 Wuppertal, Germany*

Received 19 April 2005; received in revised form 17 June 2005; accepted 21 June 2005

Abstract

The possibility of using direct chemical-ionization mass spectrometry to determine fatty alcohols in technical mixtures was examined. CH_4, i-C_4H_{10}, H_2S, NH_3 and $(CH_3)_{3-n}NH_n$ were examined as reactant gases. Methane, because its proton affinity is significantly lower than those of the alcohols, and isobutane lead to an overlapping pattern of fragment ions, which prevents evaluation of the spectra. H_2S does not form such interfering fragment ions; it forms only the quasi-molecular ions $[M-17]^+$, which serve for the quantitative detection, and $[M-1]^+$ at low intensity. The detection limits of the alcohols in methanol are between 0.007 and 0.025%. NH_3 and the amines $(CH_3)_{3-n}NH_n$ also generate no fragment ions. Instead, they form adduct ions of the form $[ROH\cdots H_{n+1}N(CH_3)_{3-n}]^+$, where $n = 0$–3. The catalytic action of the fatty alcohols in the formation of the dimers $((CH_3)_{3-n}NH_n)_2H^+$ does interfere here, however. The detection limits by NH_3-CIMS of the alcohols in a mixture are between 0.01 and 0.02%.

Keywords: Chemical-ionization mass spectrometry; Fatty alcohols; Process analysis; Reactant gases

1. Introduction

Chemical-ionization mass spectrometry (CIMS) is a versatile method for the analysis and structural determination of alcohols [1,2]. After initial studies with methane as reactant gas [3,4], the first comprehensive work with isobutane as reactant gas was carried out by Field [5]. Later work, on secondary and tertiary alcohols, was then reported by the research groups of Munson and coworkers [6] and Field and coworkers [7]. In addition, important articles have dealt with intermolecular and intramolecular substitutions of protonated alcohols [8,9], exothermicity effects in the protonation [10], theoretical calculations for the CI reactions [11,12] and analyses of alcohol with ammonia [13].

The use of mass spectrometric separation alone, without previous chromatographic separation, promises not only analysis times significantly shorter than in conventional analytical methods but the simultaneous determination of complex mixtures. Thus, a large number of compounds in gases from incinerators and from coffee roasting were analyzed by means of a portable TOF-MS with resonant laser ionization and a capillary inlet, at a time resolution of 20 ms [14,15]. Mass spectrometry for determining industrial fat products has up till now been used only in the form of GC/MS coupling for the analysis of acetylated fatty alcohols [16]. In the present work, we have adapted direct mass spectrometry for process analysis of mixtures of fatty alcohols.

2. Experimental

The analyses were carried out with a combination of Agilent gas chromatograph HP 6890, HP autosampler series 6890 and mass spectrometer HP 5973 MSD. Gas chromatograph conditions: injector, split/splitless, 320 °C; restriction capil-

---

∗ Corresponding author. Tel.: +49 231 755 4097; fax: +49 231 755 4084.
E-mail address: ligon@infu.uni-dortmund.de (A.P. Ligon).

1387-3806/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2005.06.003

lary, methyl-deactivated (length 40 cm, i.d. 50 μm); carrier gas, helium, 3.0 bar; GC temperature, 280 °C, isothermal. The Siemens automatic piston sampling valve, which is in wide-spread use in process analysis, is used for the injection. It is ideally suited for rapid online sampling of a process flow. Mass-spectrometer conditions for both full-scan and single-ion modes: interface temperature, 240 °C; ion-source temperature, 200 °C; quadrupole temperature, 106 °C; CI ion source, 20% mass-flow controller ≈ 22.7 Pa interior pressure (13.3 mPa at the electron-multiplier detector); EI ion source, 70 eV. Cylinders of methane, isobutane, hydrogen sulphide, ammonia and methyl amine gases were connected via a needle valve and a pressure reducer at the CI gas inlet directly with the CI-MFC of the mass spectrometer, and the pressure was set at 1 bar.

Most of the gases used in these experiments, especially hydrogen sulphide, are poisonous, and any experimental setup that involves their use must at all costs avoid releasing them into the laboratory or plant air. A steel tube must be provided to convey the outlet gas from the pumps and MS to a fume hood or other appropriate exhaust system.

A mixture of the linear fatty alcohols octanol to octadecanol was volatilized in the GC injector and transferred directly to the mass spectrometer by means of a restriction capillary heated by an oven. This guaranteed that the gas-phase mixture of the fatty alcohols underwent hardly any separation before it reached the mass spectrometer.

3. Results and discussion

3.1. Electron ionization

Initially, the fragmentation behaviour of an equal-weight mixture of the C8–C18 alcohols within an electron-ionization source was examined. On EI, the fatty alcohols gave the fragmentation pattern typical of hydrocarbon chains: the progressive shortening of the chain by CH_2 units can be defined as in Eqs. (1)–(3) [17].

$$F^+ = M - (17 + n \times 14) \tag{1}$$

$$F^+ = M - (18 + n \times 14) \tag{2}$$

$$F^+ = M - (19 + n \times 14) \tag{3}$$

M here is the molecular weight of the alcohols and n is the fragmentation number that takes positive integer values. The fragments described by Eq. (1) (elimination of OH or of H_2O after addition of a proton), Eq. (2) (elimination of H_2O) and Eq. (3) (elimination of H_2O and H) are characteristic of electron ionization.

Thus, no molecular ions are observed, and no specific fragments are formed that would allow the fatty-alcohol homologues to be distinguished. For this reason, the direct determination of the fatty alcohols by EI was not pursued further.

3.2. Chemical ionization

To reduce the extreme fragmentation seen in EI spectra, one often turns to chemical-ionization mass spectrometry. This ionization technique is softer than El, and the lower excess energy from the ion-molecule reaction leads to less fragmentation. If the ionization takes place by proton transfer, as it commonly does with positive chemical ionization (PCI), the extent of fragmentation depends on the difference in the proton affinities of the reaction partners [18,19].

3.2.1. Methane

The difference between the proton affinities of methane (543.5 kJ mol^{-1}) and the fatty alcohol analytes (802.6–810.2 kJ mol^{-1}) is still relatively large [12,18], and enough energy is transferred in the ionization to form numerous fragment ions, much as in EI. For this reason methane is often designated as a rather “hard” CI gas.

The secondary reactions are essentially those of the fatty alcohols with $CH_5{}^+$, the most important reactant gas ion from methane (Eqs. (4)–(8)) [20].

$$CH_5{}^+ + ROH \rightarrow ROH_2{}^+ + CH_4 \quad (M+1) \tag{4}$$

$$C_2H_5{}^+ + ROH \rightarrow ROH_2{}^+ + C_2H_4 \quad (M+1) \tag{5}$$

$$CH_5{}^+ + RCH_2OH \rightarrow RCH{=}OH^+ + CH_4 + H_2 \quad (M-1) \tag{6}$$

$$C_2H_5{}^+ + RCH_2OH \rightarrow RCH{=}OH^+ + C_2H_6 \quad (M-1) \tag{7}$$

$$CH_5{}^+ + 2ROH \rightarrow (ROH)_2H^+ + CH_4 \quad (2M+1) \tag{8}$$

The self-solvation of protonated ROH to form clusters as high as $[3M+1]^+$ was first observed by Dizidic and McCloskey [21]. Such cluster formation $[2M+1]^+$ was also observed in this work. None of the alcohols gave observable $[M+1]^+$ ions, for under the conditions used these decay immediately to $[M-1]^+$ (Eqs. (6) and (7)) or split off water to $[M-17]^+$.

$$ROH_2{}^+ \rightarrow R^+ + H_2O \quad (M-17) \tag{9}$$

It can be seen in the mass spectra of the C8–C18 alcohol mixture (Fig. 1) that only the signals $[M-1]^+$ and $[M-17]^+$ can be assigned to the individual alcohols. The fragments of these alkyl chains are not suitable for quantitative analysis, since overlapping cannot be excluded.

3.2.2. Isobutane

The proton affinity of isobutane is 677.8 kJ mol^{-1} [18], which is only about half as far from that of the fatty alcohols as is that of methane. When isobutane is used, however, the alcohols are actually protonated by the secondary ion *tert*-$C_4H_9{}^+$ the conjugate acid of isobutene (PA = 802.1 kJ mol^{-1})

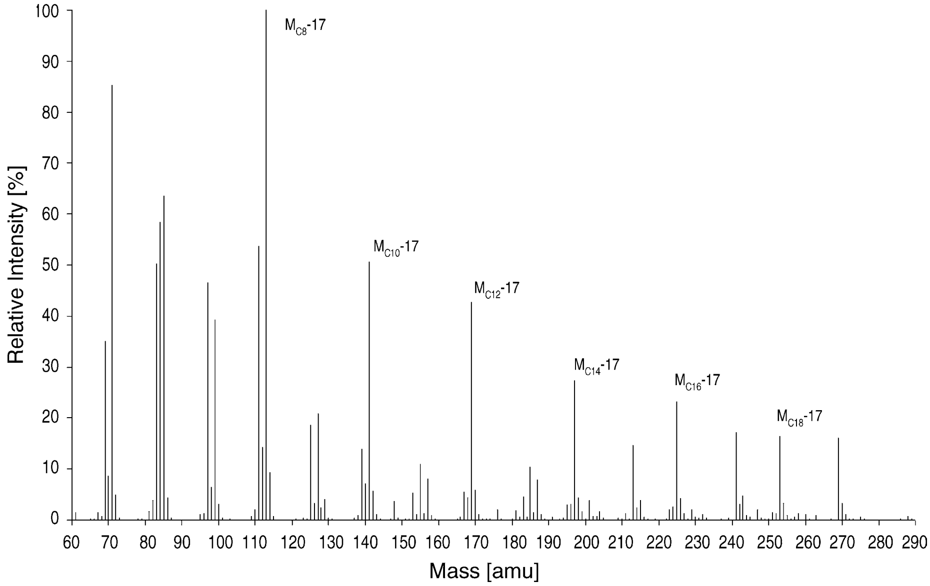

Fig. 1. Methane CI mass spectrum of a mixture of linear fatty alcohols (octanol to octadecanol).

[18]. This very small difference ought to lead to less fragmentation of the fatty alcohols.

Molecular size, stereochemistry and other structural aspects are decisive for the reactions of alcohols in an isobutane plasma [22]. The ion-molecule reactions of Eqs. (9)–(14) can be observed under various conditions (Fig. 2).

$$\mathrm{ROH} + (\mathrm{CH_3})_3\mathrm{C}^+ \rightarrow \mathrm{ROH}^+\cdots\mathrm{C(CH_3)_3} \quad (M+57) \tag{10}$$

$$\begin{aligned}&\mathrm{ROH} + \mathrm{H}^+\cdots\mathrm{H_2C{=}C(CH_3)_2}\\ &\quad\rightarrow \mathrm{R(OH)}\cdots\mathrm{H}^+\cdots\mathrm{H_2C{=}C(CH_3)_2} \quad (M+57)\end{aligned} \tag{11}$$

$$\begin{aligned}&\mathrm{R'R''CHOH} + (\mathrm{CH_3})_3\mathrm{C}^+\\ &\quad\rightarrow \mathrm{R'R''C{=}OH}^+ + i\text{-}\mathrm{C_4H_8} + \mathrm{H_2} \quad (M-1)\end{aligned} \tag{12}$$

$$\mathrm{R'R''CHOH_2}^+ \rightarrow \mathrm{R'R''C{=}OH}^+ + \mathrm{H_2} \quad (M-1) \tag{13}$$

$$\mathrm{ROH} + (\mathrm{CH_3})_3\mathrm{C}^+ \rightarrow \mathrm{R}^+ + \mathrm{HOC(CH_3)_3} \quad (M-17) \tag{14}$$

The most intense signal from the fatty alcohols is in each case that of the $[M-17]^+$ ion. In addition, the adduct $[M+57]^+$ and the dimer $[2M+1]^+$ are observed in analyses

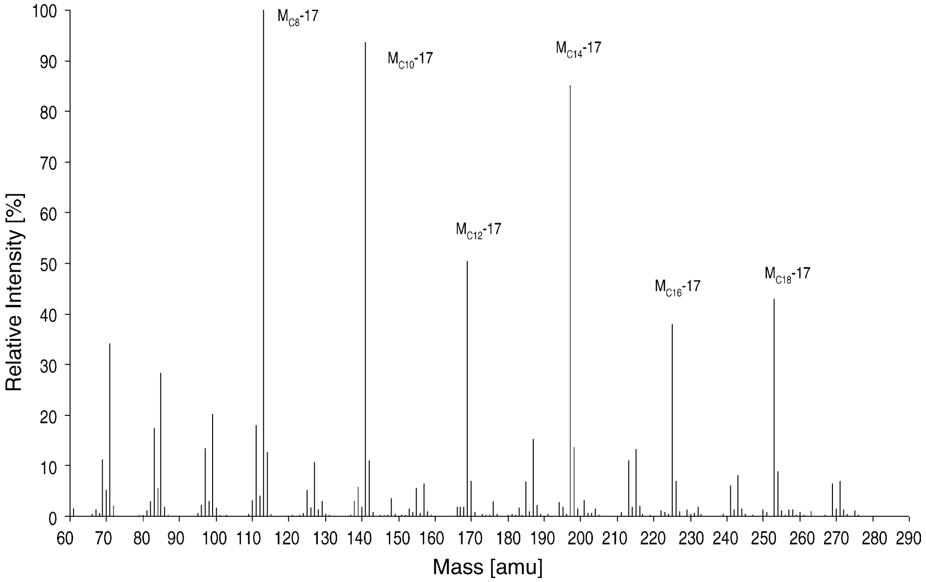

Fig. 2. Isobutane CI mass spectrum of a mixture of linear alcohols (octanol to octadecanol).

of the individual alcohols. These increase in intensity with the length of the alcohol chain because the number of collisions at the active centre decreases with the chain length; in analyses of mixtures, however, these ions become less prominent or even disappear.

The fragmentation of the hydrocarbon chains, so great with methane, is only moderate here. However, in comparison with the results from CI gases described below, it is still too great. It seems that the PA of isobutene is not a very good guide in predicting the fragmentation. This fragmentation turned out to be rather constant, so that by means of their $[M-17]^+$ ions it is possible both to identify the individual alcohols unambiguously and to quantify them in the mixture.

3.2.3. Hydrogen sulphide

Hydrogen sulphide, on account of its proton affinity (705.0 kJ mol^{-1}), aggregate state and molecular size, is an alternative to ammonia and its methyl derivatives in CIMS [12,18]. The difference between the proton affinity and that of the alcohols is large enough to prevent the formation of adducts, but is on the other hand low enough for less fragmentation to be expected.

Since chemical ionization with H_2S was still an unknown area and there was little in the literature for comparison, the ions in the CI plasma of H_2S were examined in detail, as we described in an earlier paper (Fig. 3) [23].

The signal groups appearing at a regular interval of 32 amu can be interpreted as the sulphonium cations $H_xS_n{}^+$. Like the H_3S^+ ion, the $H_2S_3{}^+$ ion here is very stable [23]. The H_3S^+ ion (35 amu), which results from proton transfer, can be regarded as the most important species for the protonation of the alcohols. Protonation of these analytes by other plasma ions is less likely (cf. Fig. 3). The extent to which the ion-molecule reactions (9) and (15)–(17) can be observed depends on the conditions selected (Fig. 4):

$$H_3S^+ + ROH \rightarrow ROH_2{}^+ + H_2S \quad (M+1) \qquad (15)$$

$$H_3S^+ + RCH_2OH \rightarrow RCH{=}OH^+ + H_2S + H_2 \quad (M-1) \qquad (16)$$

$$H_3S^+ + 2ROH \rightarrow (ROH)_2H^+ + H_2S \quad (2M+1) \qquad (17)$$

The $[M-17]^+$ ions of each fatty alcohol can be seen clearly in the mass range 113–253 amu. The lifetimes of the $[M+1]^+$ ions, from the C12 alcohol on, are sufficient for these also to appear in increasing intensity above the background. The $[M-1]^+$ ions, by contrast, protrude only slightly from the background, while the $[2M+1]^+$ adducts are observed only for the C18 alcohol, and then only at low ion-source temperatures (<175 °C) (not shown). Thus, no disturbing fragment ions need be considered in a quantitative analysis.

The calibration line (Table 1) used to determine the detection limits was based on the international standard ISO 11843-2 [24]. All together, 10–12 calibration samples in the weight concentration range ca. 0.001–0.1% were each analyzed 10 times. Methanol was used as the solvent because it gives almost no measurable reaction with H_2S. From the statistical parameters of the calibration line, detection limits of 0.007% for octanol to tetradecanol and 0.016% for octadecanol in methanol were determined.

The detection limit of 0.025% for hexadecanol is noticeably poorer and resulted from the low mass resolution of the quadrupole mass spectrometer: since it was not possible to distinguish between the H_2S plasma ion $HS_7{}^+$ and the $[M_{C16}-17]^+$ ion (both 225 amu), the detection limit for

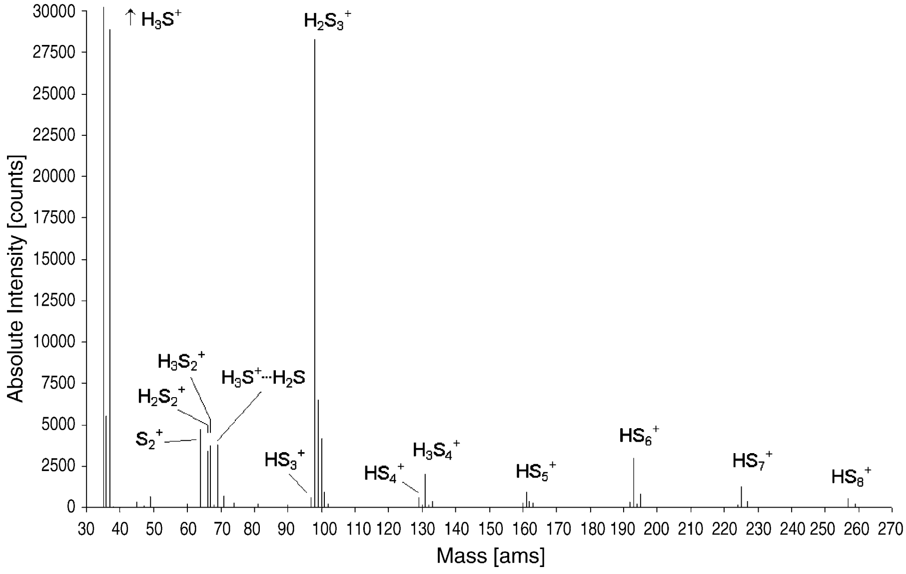

Fig. 3. Ions of the H_2S plasma. The base peak H_3S^+ is about 20 times as intense as depicted [23].

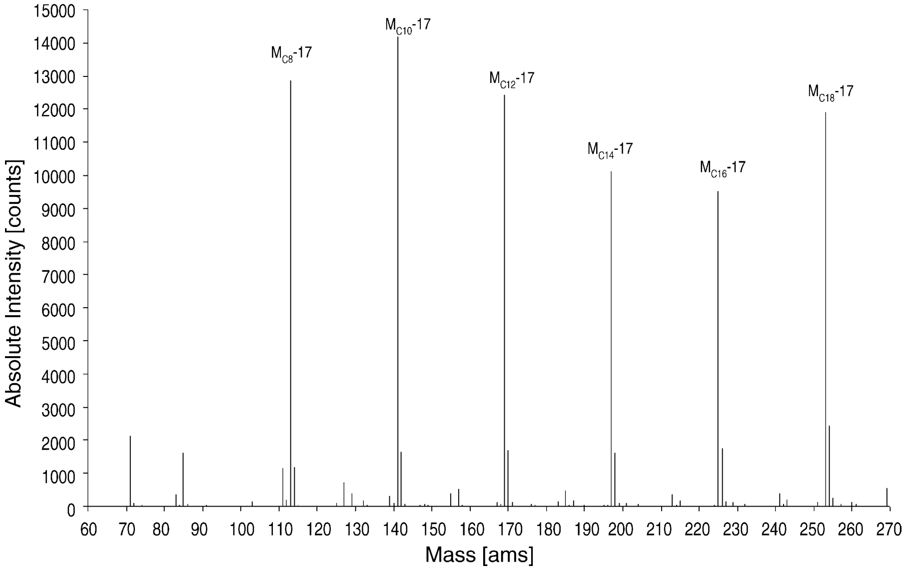

Fig. 4. CIMS spectrum of a mixture of linear fatty alcohols (octanol to octadecanol) with H_2S as reactant gas.

hexadecanol is above the intensity of the plasma ion signal. The decrease in sensitivity (Table 1) on going from octanol to octadecanol is the result of the reduced number of collisions at the active centre of the alcohols.

3.2.4. *Water*

A reviewer of the first draft of this article suggested we take a look at water as an ionizing gas. Water has a PA of 691 kJ mol^{-1}, not far from that of H_2S [12,18], and it can similarly be used for simple proton transfer. Spanel and Smith showed that the H_3O^+ ion formed from water protonates alcohols quite well and gives a good yield of $[M-1]^+$ ions [25]. Unlike H_2S, water could be used without any special safety precautions.

Unfortunately, only gases could be introduced into the mass spectrometer used for this work. A study of water as reactant gas might be rewarding; we ourselves were unfortunately not in a position to undertake it.

3.2.5. *Ammonia*

In contradistinction to the CI gases methane, isobutane and hydrogen sulphide, ammonia has a higher proton affinity (853.6 kJ mol^{-1}) than the alcohol analytes [12,18]. Because of the low PA difference, about 50 kJ mol^{-1}, proton-transfer reactions no longer take place. The ammonia reactions lead preferentially to adducts that are especially suited to quantification. The interaction of alcohols with the ions of the ammonia plasma has been studied by Gülacar et al. [26], who found that not only the ion-source temperature, but the molecular structure and the stereochemistry were important. The adducts formed are mainly $[M+18]^+$ and $[M+35]^+$. Additional reaction paths, as observed in the case of methane and isobutane, are thermodynamically unfavourable and thus not observed. The main paths can be described as in Eqs. (18)–(22) [26].

$$\mathrm{ROH} + \mathrm{NH}_4^+ \rightleftarrows \mathrm{ROH}\cdots\mathrm{H}^+\cdots\mathrm{NH}_3 \quad (M+18) \qquad (18)$$

Table 1
Performance characteristics for determining the LOD and LOQ of fatty alcohols with H_2S

Substance	Values	Regression equation[a]	R[b]	R.S.D.[c]	CV[d]	LOD[e]	LOQ[f]
Octanol	120	$y = 277092.6x + 206.7$	0.9916	0.004	9.278	0.010	0.034
Decanol	120	$y = 111553.8x - 163.8$	0.9959	0.003	6.414	0.007	0.023
Dodecanol	120	$y = 114250.0x - 521.6$	0.9817	0.006	13.766	0.015	0.050
Tetradecanol	100	$y = 42436.0x - 618.9$	0.9762	0.006	11.719	0.016	0.051
Hexadecanol	100	$y = 25429.2x - 323.7$	0.9437	0.010	18.487	0.025	0.081
Octadecanol	120	$y = 14965.8x + 102.4$	0.9881	0.005	11.052	0.012	0.041

[a] $y = m(\text{absolute intensity}\,\%^{-1}) \times (\%\ \text{weight fraction}) + b(\text{absolute intensity})$.
[b] Co-efficient of correlation.
[c] Realative standard deviation (% weight fraction).
[d] Co-efficent of variation (%).
[e] Limit of detection (% weight fraction).
[f] Limit of quantification (% weight fraction).

$$\mathrm{ROH}\cdots\mathrm{H}^{+}\cdots\mathrm{NH_3}+\mathrm{NH_3}\rightleftarrows\mathrm{ROH}\cdots\mathrm{H}^{+}\cdots\mathrm{NH_3}\cdot\mathrm{NH_3}\quad (M{+}35) \tag{19}$$

$$\mathrm{ROH}+\mathrm{NH_4^+}\rightleftarrows\mathrm{ROH_2^+}+\mathrm{NH_3}\quad (M+1) \tag{20}$$

$$\mathrm{RR'CHOH}+\mathrm{NH_4^+}\rightarrow\mathrm{RR'C{=}OH^+}+\mathrm{NH_3}+\mathrm{H_2}\quad (M-1) \tag{21}$$

$$\mathrm{ROH}+\mathrm{NH_4^+}\rightarrow\mathrm{R^+}+\mathrm{NH_3}+\mathrm{H_2O}\quad (M-17) \tag{22}$$

Reactions (18) and (19) show clearly that even alcohols can solvate $\mathrm{NH_4}^+$. At higher temperatures, clusters or adducts of the composition $[M+18+n\times17]^+$ are quickly destabilized, but a higher CI-gas pressure favours these ions. For this reason, a suitable compromise of gas pressure and temperature must be found for the CI ion source. Fig. 5 shows the ammonia CI mass spectrum of a mixture of fatty alcohols (octanol to octadecanol).

The studies of alcohol mixtures showed a continuous increase in the absolute intensity of the $[M+18]^+$ signals with increasing number of carbon atoms in the alcohol. This behaviour of the fatty alcohols makes a quantitative analysis more difficult, in that response factors are required.

The formation of clusters in ammonia spectra must be examined before the increase in intensity of the $[M+18]^+$ ions with increasing carbon number can be explained. Since the gas pressures in CI are as a rule above 20 Pa, the main ion formed from ammonia is $\mathrm{NH_4}^+$ [27,28]. Self-solvation, however, leads to some clusters, which become prominent at high CI-gas pressures as a result of collisional stabilization. High temperatures operate in the opposite direction, favouring the formation of $\mathrm{NH_4}^+$. Under the conditions used in this work, the solvation shell can consist of as many as four molecules of $\mathrm{NH_3}$ (Eq. (23)).

$$\mathrm{NH_4}^+\cdots(n-1)\mathrm{NH_3}+\mathrm{NH_3}\overset{+\Delta p}{\rightleftarrows}\mathrm{NH_4}^+\cdots(n)\mathrm{NH_3}\quad (n=1\text{–}4) \tag{23}$$

The plasma is composed largely of the ions $\mathrm{NH_4}^+$, $\mathrm{NH_4}^+\cdots\mathrm{NH_3}$ (35 amu) and $\mathrm{NH_4}^+\cdots2\mathrm{NH_3}$ (52 amu). Because of their lower concentration in the plasma, the solvated ions of the third and fourth stages ($\mathrm{NH_4}^+\cdots3\mathrm{NH_3}$; $\mathrm{NH_4}^+\cdots4\mathrm{NH_3}$) can be neglected.

To improve our theoretical understanding of the reactions taking place in the ionization of the fatty alcohols, the intensities of key ions in the ion source were examined as a function of time. With decanol as an example, the ions $\mathrm{C_{10}H_{21}OH}\cdots\mathrm{NH_4}^+$ (176 amu) and $\mathrm{C_{10}H_{21}OH}\cdots\mathrm{N_2H_7}^+$ (193 amu) were determined along with $\mathrm{NH_4}^+$ (18 amu) and $\mathrm{N_2H_7}^+$ (35 amu) in single-ion mode (SIM) (Fig. 6).

Before decanol enters the ion source, $\mathrm{NH_4}^+$ and $\mathrm{N_2H_7}^+$ are present in a constant, though pressure-dependent ratio (Eq. (24)).

$$\mathrm{NH_3}+\mathrm{NH_4}^+\rightleftarrows[\mathrm{NH_3}\cdots\mathrm{NH_4}]^+ \tag{24}$$

In the presence of the alcohol, the intensity of $\mathrm{NH_4}^+$ falls as expected, while that of $[M+18]^+$ increases, in accordance with Eq. (25).

$$\mathrm{ROH}+\mathrm{NH_4}^+\rightleftarrows[\mathrm{ROH}\cdots\mathrm{NH_4}]^+ \tag{25}$$

At the same time, there is a sudden increase in the $\mathrm{N_2H_7}^+$ ions. This can be explained by a rapid, temperature-dependent reaction of $[\mathrm{ROH}\cdots\mathrm{NH_4}]^+$ with $\mathrm{NH_3}$, corresponding to Eqs. (26) and (27). The newly formed $[M+35]^+$ ions decompose to the alcohol and $\mathrm{N_2H_7}^+$. That leads to an increase in $\mathrm{N_2H_7}^+$,

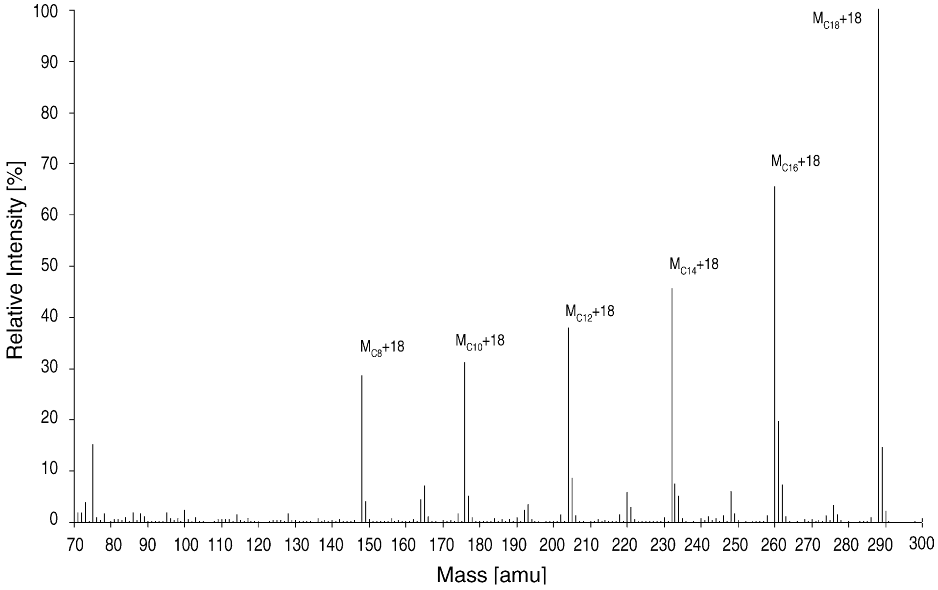

Fig. 5. $\mathrm{NH_3}$ CI mass spectrum of an equimolar mixture of linear fatty alcohols (octanol to octadecanol).

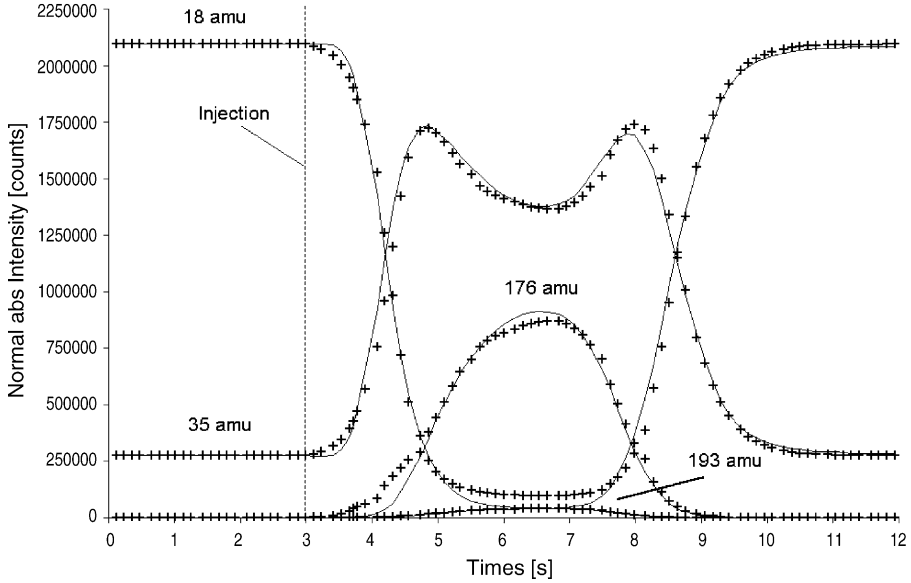

Fig. 6. Comparison over time of the experimental and calculated intensities of the ions NH_4^+ (18 amu), $N_2H_7^+$ (35 amu), $C_{10}H_{21}OH\cdots NH_4^+$ (176 amu) and $C_{10}H_{21}OH\cdots N_2H_7^+$ (193 amu) (legend: line: experiment; +: simulated values).

while the alcohol is available to participate, as a kind of catalyst, in a further cycle. Clues to such a catalytic reaction sequence in the case of *tert*-pentanol were discovered by Cody in the course of a low-pressure CI-FTMS study [29].

$$[ROH\cdots NH_4]^+ + NH_3 \rightleftarrows [ROH\cdots NH_4\cdots NH_3]^+ \quad (26)$$

$$ROH + [NH_3\cdots NH_4]^+ \rightleftarrows [ROH\cdots NH_4\cdots NH_3]^+ \quad (27)$$

The path of the reaction for decanol was simulated on the basis of Eqs. (24)–(27) and the experimental results (Fig. 6). The simulation was done iteratively in accordance with the Levenberg–Marquardt algorithm [30]. For a numerical solution, the differential equations with estimated parameters for the mechanism above were integrated as a function of time with the program FACSIMILE [31]. The simulated course of the reaction agrees with the experimental course in Fig. 6 for all the ions involved (NH_4^+, $N_2H_7^+$, $[C_{10}H_{21}OH\cdots NH_4]^+$ and $[C_{10}H_{21}OH\cdots N_2H_7]^+$). At the same time, the lifetimes of the ions in the forward and reverse reactions were adjusted. With these data, it was possible to predict the relative rate constants. Thus, the rate constant for the formation of $[C_{10}H_{21}OH\cdots NH_4]^+$ (Eq. (25)) is larger than that for the formation of $[C_{10}H_{21}OH\cdots N_2H_7]^+$ (Eq. (27)), $k^{(25)}/k^{(27)} = 5.6$. At the same time, the rate constant for the decomposition of the $[M_{C10} + 35]^+$ adduct (Eq. (27)) is larger than that for the decomposition of the $[M_{C10} + 18]^+$ adduct (Eq. (25)), $k_{-1}^{(27)}/k_{-1}^{(25)} = 76.3$. According to the results, the ratio of the formation rates of $[M + 18]^+$ increases exponentially as one goes from octanol to octadecanol. It should be noted further that the number of collisions at the OH group decreases in that sequence. The lower alcohols thus have a far greater catalytic influence on the formation of $N_2H_7^+$ (Eqs. (25)–(27)) and thereby form less and less measurable amounts of the $[M + 18]^+$ ion. The very small $[M + 18]^+$ signal that results for octanol (about a tenth as large as for octadecanol) is more subject to the background noise and makes the determination of low concentrations difficult.

In contrast to complex mixtures, binary mixtures of fatty alcohols allow a quantitative analysis without mathematical complications.

Fig. 7 is an example of the calibration of the binary mixture octanol and decanol. Calibration for process control is straightforward here because the relative intensities of ions from any two neighbouring alcohols are similar and the formation of $N_2H_7^+$ does not disturb very much.

The detection limits determined according to ISO 11843-2 [24] for such binary mixtures of all six alcohols are between 0.01 and 0.02%. The average determination limit of 0.04% is thus sufficient for quantitative determination within the framework of process analysis.

3.2.6. *Methyl amines*

The increase in the intensity of the dimer when the fatty alcohol enters the ion source was also observed in the case of the monomethyl and dimethyl amines PA = 899.0 and 929.5 kJ mol^{-1}) [12,18]. The dimer of trimethylamine (PA = 948.9 kJ mol^{-1}) [18] was below the limit of detection of the spectrometer at the temperature used. These catalytic reactions of the *n*-alcohols with the methyl amines are given in Eqs. (28) and (29).

$$ROH + (CH_3)_{3-n}NH_{n+1}{}^+ \underset{+\Delta T}{\rightleftarrows} [ROH\cdots H_{n+1}N(CH_3)_{3-n}]$$
$$(n = 0\text{–}3) \quad (28)$$

$$[ROH\cdots H_{n+1}N(CH_3)_{3-n}]^+(CH_3)_{3-n}NH_n \underset{+\Delta T}{\rightleftarrows} ROH$$
$$+((CH_3)_{3-n}NH_n)_2H^+ \quad (29)$$

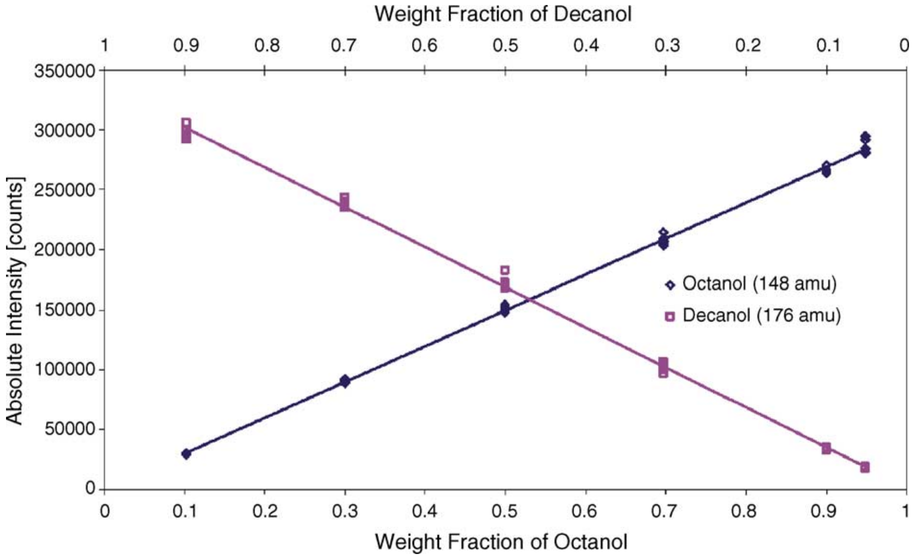

Fig. 7. Calibration of the absolute intensity of $[M + 18]^+$ from octanol and decanol in a C8/C10 mixture as a function of the weight fraction of octanol.

The catalytic activity of the fatty alcohols here lies in their ability to reduce the activation energy for formation of the dimeric methyl amines. During the formation of the quasi-molecular ions, there is always an increase in the concentration of the undesirable reactant gas dimers.

The intensity sequence $I_{M+18} > I_{M+32} > I_{M+46} > I_{M+60}$ derived from the spectra of the alcohol adducts correlates inversely with the number of methyl groups on the nitrogen. Switching the CI gas from ammonia to the methyl amines thus does not raise the intensity of the alcohol adducts, and a quantitative analysis is more difficult than with ammonia.

The two-molecule clusters described here would actually be formed in a three-body reaction. The carrier gas helium, a constant in the ion source, acts as the third body, but was not used in the simulation of the NH_3 reactions. The good agreement between experiment and simulation validated this modus operandi.

4. Conclusion

Comparison of the mass spectra presented, as obtained with various ion sources (EI, CI) and various CI gases (methane, isobutane, hydrogen sulphide, ammonia and methyl amines), reveals that without chromatographic separation the fatty alcohols can only be determined quantitatively by means of their quasi-molecular ions ($[M - 17]^+$ or $[M + 18]^+$).

The use of CI gases methane and isobutane (effective proton affinity lower than that of the fatty alcohols) makes it more difficult to evaluate the quasi-molecular ions formed because of overlapping of fragment ions of the alkyl chain.

The ion-molecule reactions taking place in the ion source are very complex with ammonia, so that only binary mixtures of the fatty alcohols are simple enough to be quantitated sufficiently. Since the extent of the interfering catalysis to $N_2H_7^+$ decreases in the sequence octanol to octadecanol, no simple dependence of the signal intensity on the weight concentration is to be expected. Methyl amines give similar results.

With sufficient mass-spectrometric resolution of HS_7^+ (225.81 amu) and $C_{16}H_{33}^+$ ($[M_{C16} - 17]^+$; 225.26 amu), the best sensitivities would be attainable with hydrogen sulphide. The H_2S CIMS technique is thus capable of following and controlling the concentrations of fatty alcohols online in industrial systems. With the right mass spectrometer, the time resolution for the analyses might be as low as 20 ms.

In a practical industrial situation, the composition of a product mixture may change constantly to favour one or more compounds. In order to simulate this, mixtures with increasing content of the longer-chained alcohols were analysed. H_2S CIMS proved to be an appropriate method for analysing and directing the industrial alcohol production. The measurement error for a mixture of all alcohols approximated 0.01 wt.%, with a recovery near 100% and without any sample preparation before the direct injection. The linearity of the calibration ranges from the LOD up to 100% weight fraction.

Acknowledgements

We are grateful to Henkel KGaA, Germany, for financial support of this work and to Dr. Walter V. Turner for helpful discussions and suggestions.

References

[1] F.H. Field, Acc. Chem. Res. 1 (1968) 42.
[2] W.J. Richter, H. Schwarz, Angew. Chem. Int. Ed. 17 (1978) 424.
[3] M.S.B. Munson, J. Am. Chem. Soc. 87 (1965) 5313.
[4] M.S.B. Munson, F.H. Field, J. Am. Chem. Soc. 88 (1966) 2621.

[5] F.H. Field, J. Am. Chem. Soc. 92 (1970) 2672.
[6] B.L. Jelus, R.K. Murray, M.S.B. Munson, J. Am. Chem. Soc. 97 (1975) 2362.
[7] S.G. Lias, A. Viscomi, F.H. Field, J. Am. Chem. Soc. 96 (1974) 359.
[8] J.L. Beauchamp, M.C. Caserio, T.B. McMahon, J. Am. Chem. Soc. 96 (1974) 6243.
[9] J.G. Liehr, G.A. Brenton, J.H. Beynon, J.A. McCloskey, W. Blum, W.J. Richter, Helv. Chim. Acta 64 (1981) 835.
[10] J.A. Herman, A.G. Harrison, Can. J. Chem. 59 (1981) 2125.
[11] J. Jalonen, J. Taskinen, C. Gildewell, Int. J. Mass Spectrom. Ion Phys. 46 (1983) 243.
[12] A.P. Ligon, J. Phys. Chem. A 104 (2000) 8739.
[13] Y.Y. Lin, L.L. Smith, Biomed. Mass Spectrom. 5 (1978) 604.
[14] H.J. Heger, R. Zimmermann, R. Dorfner, M. Beckmann, H. Griebel, A. Kettrup, U. Boesl, Anal. Chem. 71 (1999) 46.
[15] R. Zimmermann, H.J. Heger, R. Dorfner, U. Boesl, A. Kettrup, Resonance Ionization Spectroscopy: Ninth International Symposium, vol. 454, 1998, p. 59.
[16] I. Hormann, H. Traitler, J. Aeschlimann, J. High Res. Chromatogr. 12 (1989) 308.
[17] R.A. Brown, W.S. Young, N. Nicolaides, Anal. Chem. 26 (1954) 1653.
[18] E.P.L. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413.
[19] D.H. Aue, M.T. Bowers (Eds.), Gas Phase Ion Chemistry, Academic Press, 1979, p. 1.
[20] B.J. Millard, Quantitative Mass Spectrometry, Heyden, London, 1978.
[21] I. Dzidic, J.A. McCloskey, J. Am. Chem. Soc. 93 (1971) 4955.
[22] F.J. Winkler, F.O. Giilacar, F. Mermoud, A. Buchs, Helv. Chim. Acta 66 (1983) 929.
[23] A.P. Ligon, S. Gäb, Int. J. Mass Spectrom. 243 (2005) 241.
[24] ISO 11843-2, Capability of Detection—Part 2: Methodology in the Linear Calibration Case, issued May 2000.
[25] P. Spanel, D. Smith, Int. J. Mass Spectrom. Ion Proc. 167/168 (1997) 375.
[26] F.O. Gülacar, F. Mermoud, F.J. Winkler, A. Buchs, Helv. Chim. Acta 67 (1984) 488.
[27] M.S.B. Munson, J. Phys. Chem. 70 (1966) 2034.
[28] R.A. Hancock, M.G. Hodges, Int. J. Mass Spectrom. Ion Phys. 46 (1983) 329.
[29] R.B. Cody, Anal. Chem. 61 (1989) 2511.
[30] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, Numerical Recipes in C: The Art of Scientific Computing, second ed., Cambridge University Press, Cambridge, UK, 1992.
[31] A.R. Curtis, W.P. Sweetenham, FACSIMILE Process and Chemical Reaction Modeller, AEA Technology Harwell Laboratories, Oxfordshire, UK, 1994.