

Water solubilization of ethanol and BTEX from gasoline: on-line monitoring by membrane introduction mass spectrometry

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The solubilization of ethanol and the aromatic hydrocarbons benzene, toluene and the isomeric ethylbenzene and xylenes (BTEX) in water in contact with commercial samples of ethanol-containing Brazilian gasoline was monitored on-line by membrane introduction mass spectrometry (MIMS) and BTEX and ethanol concentrations in water after prolonged contact were measured by flow injection analysis (FIA) coupled with MIMS (FIA–MIMS). The cosolvent effect of ethanol, which is known to increase BTEX solubility in water, was also found to speed up BTEX solubilization as compared with ethanol-free gasoline. The ethanol cosolvent effect was also compared with that of methyl tert-butyl ether (MTBE). Chemometric multivariate analysis applied to FIA–MIMS mass spectra of the ethanol–BTEX aqueous solutions formed after prolonged contact with gasoline samples showed that identical samples cluster closely whereas small variances in BTEX composition occurring among and within the three different types of ethanol-containing Brazilian gasoline are easily detected as they cause great dispersion in the chemometric plots.

Introduction

Groundwater contamination by fuel is a serious environmental problem. Fuel spills or leaking underground fuel storage tanks contaminate the ground and the more water-soluble fuel constituents eventually contaminate groundwater resources. Major concern centers upon groundwater contamination by the toxic and water-soluble BTEX aromatic hydrocarbon components of gasoline: benzene, toluene and the isomeric ethylbenzene and *o*-, *m*- and *p*-xylene.¹ BTEX display high pollution potential owing to their relatively high concentration in gasoline and solubility in water and chronic toxicity.² Migration of BTEX from gasoline to groundwater or other potential drinking water resources is therefore an issue of major environmental concern.

Brazilian gasoline is unique since it contains 25–30% of ethanol and ethanol should have an important cosolvent effect on the speed of BTEX solubilization and final BTEX concentrations³ in groundwater in contact with ethanol-containing gasolines. The addition of polar organic solvents that are completely miscible or highly soluble in water such as methanol, ethanol and methyl *tert*-butyl ether (MTBE) to a mixture of hydrocarbons and water results in a cosolvent effect that increases the aqueous concentration of hydrocarbons.⁴ Ethanol has also been shown to affect the biodegradation of BTEX in water.³

To monitor groundwater contamination by fuel, several chemical contaminants must be quantitated at trace level concentrations in complex water matrices with considerable potential for interference from other trace impurities.⁵ Membrane introduction mass spectrometry (MIMS)⁶ is a powerful technique for selective and real-time monitoring of volatile organic compounds (VOCs)⁷ or semi-volatile organic compounds (SVOCs)⁸ directly from aqueous solutions. In MIMS, the introduction of an analyte into the mass spectrometer occurs *via* selective transport through a silicone membrane. The hydrophobicity of the silicone membrane and its high permea-

bility to apolar or less polar compounds allow the efficient and selective permeation of VOC contaminants from water, which greatly reduces sample complexity. The extraction and pre-concentration of the analytes by the membrane is performed rapidly and simultaneously. MIMS is therefore an attractive technique for on-site environmental analysis of water resources contaminated by VOCs⁹ and many SVOCs.⁸ MIMS analysis is also rapid and therefore applicable to on-line continuous monitoring and compatible with flow injection analysis (FIA)¹⁰ methods of sample handling. The FIA–MIMS coupling¹¹ displays most of the major advantages of MIMS plus higher speed, simplicity of the experimental set-up and economy of sample and reagents.

Gasoline is a complex mixture of mainly hydrocarbons (Table 1), the composition of which depends on the petroleum type and production method.² BTEX are aromatic hydrocarbons commonly found in gasoline (Table 2) and are those which migrate more efficiently to groundwater.¹²

In this study, we tested the applicability of MIMS to monitor the solubilization of ethanol and BTEX in water in contact with different types of ethanol-containing gasoline samples commercially available in Brazil. MIMS monitoring was used to evaluate the cosolvent effect of ethanol in the initial BTEX solubilization as compared with ethanol-free and MTBE-containing gasoline samples. FIA–MIMS analyses were then performed to determine the ethanol and BTEX concentrations in water after prolonged contact with the gasoline sample.

Table 1 Typical composition of additive-free gasoline

Constituents	Concentration (% v/v)
Alkanes (C ₃ –C ₁₀ n-alkanes and C ₄ –C ₁₃ isoalkanes) and cycloalkanes (C ₅ –C ₁₃)	56
Alkenes (C ₂ –C ₁₂)	10
Aromatic hydrocarbons (C ₆ –C ₁₂)	33
Polycyclic aromatic hydrocarbons (PAHs)	1

Chemometric multivariate analysis was then applied to the FIA-MIMS mass spectra to evaluate the ability of such an approach to detect variances of the BTEX composition in the gasoline-contaminated water.

The principal component analysis¹³ (PCA) employed in this work is the fundamental basis of most multivariate methods in multivariate analysis.¹⁴ Multivariate analysis is used to investigate the correlation between variables and to explore the structure of large data sets; it organizes the data *via* condensation into a reduced number of variables, which are more easily comprehended. For classification based on similarity or for determination of an unknown variable *y* (*e.g.*, concentration), many instrumental variables such as absorption, time and intensity values can be used simultaneously.

In brief, PCA¹³ is a method used to decompose a matrix **X** of rank *r* in a sum of *r* matrices of rank 1:

$$\mathbf{X} = \mathbf{M}_1 + \mathbf{M}_2 + \mathbf{M}_3 + \dots + \mathbf{M}_r$$

Rank is a number expressing the true underlying dimensionality of a matrix. The rank 1 matrices, **M_r**, can be written either as outer products of two vectors, a score *t_r*, and the loading *p_r'*:

$$\mathbf{X} = t_1 p_1' + t_2 p_2' + \dots + t_r p_r'$$

or in the matrix form: $\mathbf{X} = \mathbf{TP}'$ where **P'** is made up with *p'* as rows and **T** with *t* as columns.

Experimental

Aqueous standard solutions of BTEX were prepared by serial dilutions from 100 mg L⁻¹ stock standard BTEX solutions in methanol. The gasoline samples used in the MIMS solubilization experiments (g0, c0, a0 and p0) were provided by Shell do Brasil (Campinas, SP, Brazil): g0 was an ethanol- and additive-free gasoline sample; c0 was an ethanol-containing additive-free gasoline sample of the Brazilian 'comum' type (*ca.* 22% ethanol and 0.7% water); a0 was an ethanol- and additive-containing gasoline sample of the 'aditivada' type (*ca.* 22% ethanol, 0.7% water and variable amounts of additives); and p0 was a higher octane ethanol- and additive-containing gasoline sample of the 'premium' type (*ca.* 22% ethanol, 0.7% water and variable amounts of octane enhancers). For the classification and quantitation experiments, samples of the three main gasoline types commercially available in Brazil (type cn, an and pn; *n* = 1–19) were collected at random directly from various fuel stations in the city of Campinas, SP, Brazil.

A single-quadrupole ABB Extrel (Pittsburgh, PA, USA) mass spectrometer using 70 eV electron ionization (EI) and a standard MIMS probe¹⁵ with a 125 μm silicone sheet membrane¹⁶ (Silastic 500-3 from Dow Corning) were used. Monitoring of gasoline solubilization in water was performed by adding 10 mL of the gasoline sample at the top of 200 mL of de-ionized water contained in a 500 mL Erlenmeyer flask. The mixture was gently stirred and the aqueous mixture was then pumped continuously through the standard MIMS probe using a multi-channel peristaltic pump at a flow rate of 2 mL min⁻¹. Benzene-d₆ (*m/z* 84) was used as an internal standard for response calibration. All experiments were performed at room temperature (22 ± 2 °C) with constant stirring. The ethanol and BTEX (and also MTBE) solubilization was followed on-line by selected ion monitoring (SIM) of characteristic ions formed by

Table 2 Water solubility and common concentrations in gasoline of BTEX

BTEX	Water solubility/mg L ⁻¹	Gasoline concentration (% v/v)
Benzene	1740–1860	2–5
Toluene	500–627	6–7
Ethylbenzene	131–208	5
Xylenes	167–196	6–7

70 eV EI: ethanol (*m/z* 45); benzene (*m/z* 78), toluene (*m/z* 92), ethylbenzene and the xylenes (*m/z* 106) and MTBE (*m/z* 73).

For the quantitation and classification experiments, 2.5 mL of gasoline were added at the top of 50 mL of de-ionized water and the two-phase system was allowed to rest for 24 h at 22 ± 2 °C. To minimize any matrix effects in BTEX membrane permeation and MS ionization that could result from the presence of ethanol in water, the BTEX standard solutions used in the quantitation experiments were doped with 1.3% of ethanol (50 mL of water after prolonged contact with 2.5 mL of ~25% ethanol-containing gasoline contains nearly 1.3% of ethanol; see Table 3).

The concentrations of BTEX in the aqueous phase were measured using the FIA-MIMS system shown in Fig. 1: a stream of de-ionized water (W) was pumped continuously through the system by a multi-channel peristaltic pump at a flow rate of 2 mL min⁻¹. The BTEX-containing aqueous solution (S) was then pumped through the system at a flow rate of 2 mL min⁻¹ and a 500 μL plug of the aqueous BTEX sample contained in the FIA loop tubing (L) was injected into the water stream using the FIA valve (V). Mass spectra in the *m/z* 40–150 range were then collected for the classification analysis whereas SIM was performed for quantitation.

Results and discussion

Water solubilization of ethanol and BTEX monitored by MIMS

Fig. 2 shows a typical MIMS 70 eV EI mass spectrum of water after prolonged contact with an ethanol-containing gasoline sample. Considering the complexity of gasoline composition (Table 1), the mass spectrum in Fig. 2 is relatively simple owing to selective permeation of the less polar and lighter VOCs

Table 3 BTEX and ethanol concentrations in water (50 mL) as determined by FIA-MIMS using SIM after 24 h of contact with 2.5 mL of ethanol-containing gasoline samples at room temperature

Water contaminant	Concentration range
Benzene	7.5–20.4 mg L ⁻¹
Toluene	0.9–24.9 mg L ⁻¹
Xylenes	4.8–19.1 mg L ⁻¹
Ethanol	1.2–1.5% ^a

^a These concentrations equate to 21–34% ethanol concentration in gasoline.

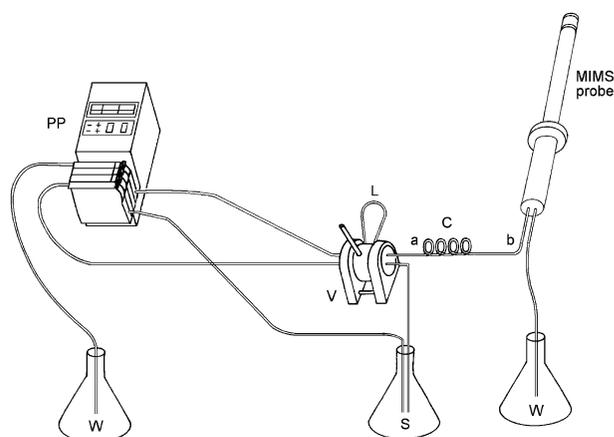


Fig. 1 Experimental set-up used for the integrated on-line derivatization FIA-MIMS determination of BTEX in water. PP, peristaltic pump; V, FIA valve; C, glass mixing coils; L, FIA loop (defines the sample volume), S, BTEX aqueous sample; W, waste. Lengths *a* and *b* are 15 and 30 cm, respectively. Adapted from ref. 11g.

through the hydrophobic silicone membrane. Although relative peak heights naturally have no direct correlation with concentrations in gasoline owing to substantial differences in membrane permeabilities and ionization efficiencies, the mass spectrum displays ions that are qualitatively correlated with major water-soluble VOC constituents of gasoline and those from ethanol (m/z 46 and 45) and BTEX (m/z 77, 78, 91, 92, 105 and 106) are the ones most easily recognized. Note, for instance, that the ethanol concentration in the gasoline-contaminated water is far greater than those of BTEX (Table 2), but the peak heights for the characteristic ethanol and BTEX ions display relatively close abundances because the more polar ethanol permeates through the hydrophobic silicone membrane much less efficiently than BTEX.⁶ This simplifies combined BTEX and ethanol quantitation, as discussed below. Two other major ions indicate solubilization of a mixture of isomeric alkenes and cyclic alkanes of C_5H_{10} (m/z 70) and C_6H_{12} (m/z 84) compositions, whereas m/z 55 is a common and often abundant fragment ion in the 70 eV EI mass spectra of these hydrocarbons. Characteristic ions were selected to monitor ethanol and BTEX: m/z 45 for ethanol, m/z 78 for benzene, m/z 92 for toluene and m/z 106 for the combined monitoring of the isomeric ethylbenzene and the xylenes.

Fig. 3 shows the profile of on-line SIM-MIMS monitoring of ethanol and BTEX water solubilization from the four 'standard' Brazilian gasoline samples (g0, c0, a0 and p0) during the first 90 min of water-gasoline contact at room temperature. The profile for the ethanol- and additive-free g0 gasoline sample [Fig. 3(a)] shows the slowest solubilization of benzene (m/z 78), toluene (m/z 92) and ethylbenzene/xylenes (m/z 106) and, as expected for this ethanol-free gasoline sample, m/z 45 is nearly undetectable. The profile for the ethanol-containing additive-free c0 gasoline sample [Fig. 3(b)] shows a rapid increase and leveling of the m/z 45 ion owing to rapid solubilization of ethanol. The cosolvent effect of ethanol is evident since BTEX solubilize faster with their concentrations nearly flattening after 90 min of water-gasoline contact. The profile for the ethanol- and additive-containing a0 gasoline sample [Fig. 3(c)] is similar to that of the c0 gasoline sample [Fig. 3(b)]. The profile for the ethanol-containing higher octane p0 gasoline sample is, however, distinct; benzene (m/z 78), ethanol (m/z 45) and ethylbenzene/xylene (m/z 106) solubilization follows similar trends to those observed in Fig. 3(b) and (c), but much higher concentrations of toluene are detected during the initial 90 min of monitoring, probably as a consequence of its substantially higher concentration in the p0 sample.

The cosolvent effect of ethanol, which affects the solubilization of hydrocarbons in water, has already been studied,³ and an increase in benzene solubility in water of *ca.* 18% was observed for a 0.025 mole fraction of ethanol in water.^{3d} The present results for MIMS on-line monitoring show that ethanol also speeds up considerably BTEX solubilization in water, hence both faster solubilization and higher BTEX concentrations

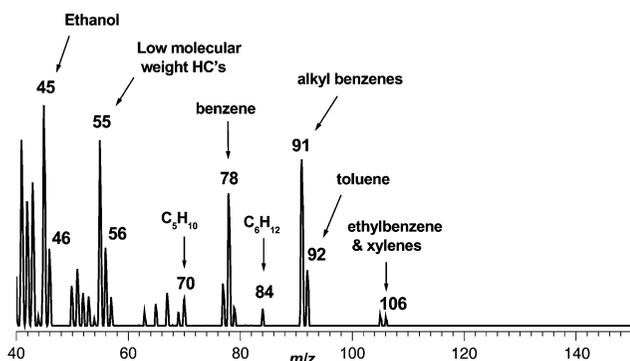


Fig. 2 Typical MIMS 70 eV EI mass spectrum of a water sample after prolonged contact with ethanol-containing gasoline.

should be observed for groundwater in contact with ethanol-containing gasolines.

MTBE cosolvent MIMS monitoring

BTEX solubilization in water from an MTBE-containing¹⁷ gasoline sample was also evaluated. The sample was prepared by adding 4% v/v of MTBE¹⁸ to the ethanol- and additive-free g0 gasoline sample and water solubilization was monitored by MIMS as described before. Clearly, the cosolvent effect of MTBE in speeding up BTEX solubilization in water is much more pronounced than that of ethanol. For the *ca.* 25% ethanol-containing gasoline sample C0, the BTEX concentrations start to level off after ~90 min of water-gasoline contact [Fig. 3(b)]; for the 4% MTBE-containing sample (Fig. 4), leveling occurs just after 20 min.

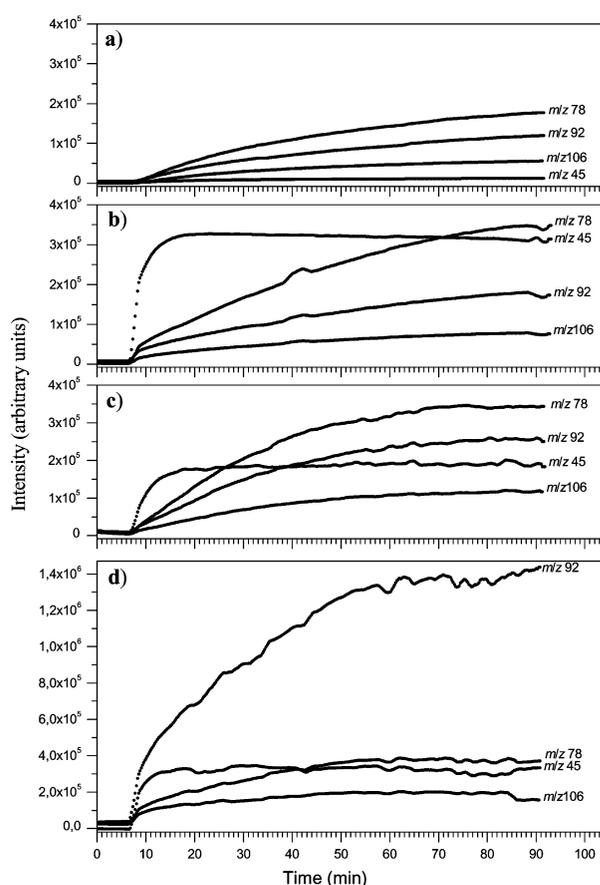


Fig. 3 MIMS-SIM on-line monitoring of water solubilization of ethanol (m/z 45), benzene (m/z 78), toluene (m/z 92) and ethylbenzene/xylenes (m/z 106) from gasoline samples of type (a) g0, (b) c0, (c) a0 and (d) p0.

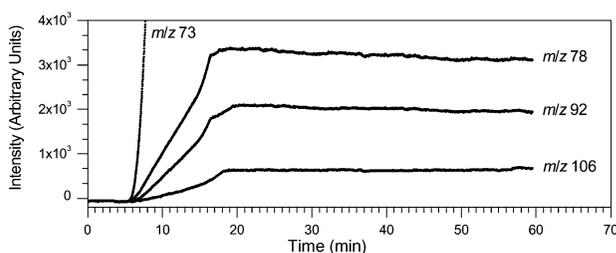


Fig. 4 SIM-MIMS on-line monitoring of the water solubilization of MTBE (m/z 73), benzene (m/z 78), toluene (m/z 92) and ethylbenzene/xylenes (m/z 106) from an MTBE-containing (4% v/v) gasoline sample.

FIA-MIMS analysis

FIA-MIMS was applied to quantitate ethanol and BTEX in water and standard aqueous solutions of ethanol (15–40%) and standard 1.3% ethanol-containing aqueous BTEX solutions (5.0–40.0 mg L⁻¹) were prepared and analyzed. Fig. 5, which displays the SIM profile obtained for the standard solutions, demonstrates the good linearity of FIA-MIMS quantitation ($r = 0.996$ – 0.998). Then, BTEX and ethanol were simultaneously determined in water after 24 h of contact at room temperature with each of the 19 ethanol-containing gasoline samples from the three types commercially available in Brazil: cn, an and pn ($n = 1$ – 19).

The ethanol and BTEX concentrations (Table 3) vary within relatively broad ranges, thus reflecting the diversity of the BTEX composition of gasoline, which also varies in different areas of the country and throughout the year. The gasoline composition may change daily depending on the supplier and changes in refinery operating conditions and the addition of different additives.

Chemometric multivariate analysis

Mass spectra in the m/z 40–150 range were also collected using the FIA-MIMS system. The PCA method was then employed to monitor the variance of BTEX composition among and within the three types of Brazilian gasolines (cn, an and pn; $n = 1$ – 19) based on the VOC composition in water after prolonged gasoline–water contact. The spectra were normalized and mean-centered and the PCA method was employed. Table 4 shows percentage variance explained by each of the six principal components and that PC1 plus PC2 are able to explain ~90% of the data variance.

Fig. 6 shows the plot of the scores of the first (PC1) versus the second principal component (PC2) for the 19 samples analyzed. Great dispersion is observed and samples, even those for the

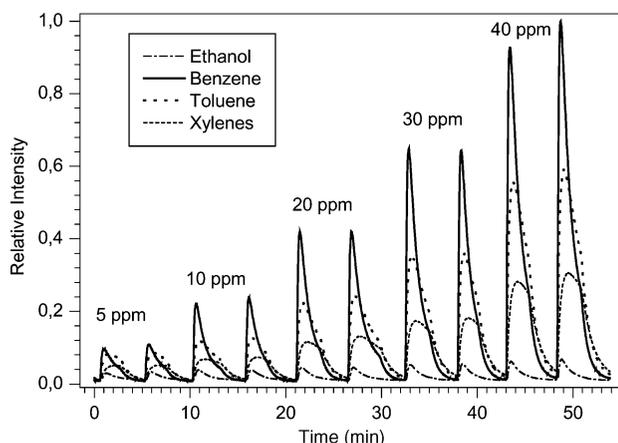


Fig. 5 FIA-MIMS monitoring using SIM for successive injections of aqueous solutions of ethanol, benzene, toluene and xylenes at various concentrations.

Table 4 Percentage variance captured by PCA for the six principal components

Principal component	Variance captured for each PC (%)	Total variance captured (%)
1	75.92	75.92
2	13.27	89.19
3	5.62	94.80
4	2.19	96.99
5	0.96	97.95
6	0.74	98.69

same gasoline type, are placed at random. The same dispersion is observed for PC1 versus PC3. PCA processing of MIMS mass spectra taken from the same sample shows >95% reproducibility, hence the great dispersion among different samples indicates that FIA-MIMS with chemometric analysis is able to detect rapidly and efficiently the variances of the composition of the water-soluble components of the Brazilian ethanol-containing gasolines, among and even within samples of the same gasoline type sampled in a restricted area and within a very narrow time frame.

Fig. 7 shows plots of the loadings for PC1 and PC2. PC1 [Fig. 7(a)], which explains ~76% of the data variance, displays the highest loading for m/z 41, 55 and 78. The major influence on sample separation by these ions can be seen in Fig. 6, since

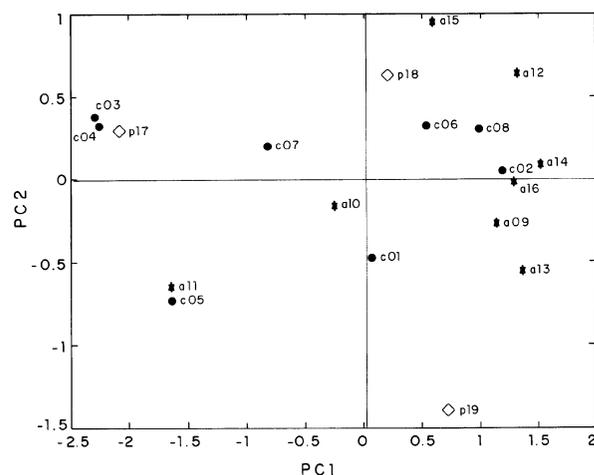


Fig. 6 Plot of the scores of PC1 (75.92%) versus PC2 (13.27%) for gasoline samples.

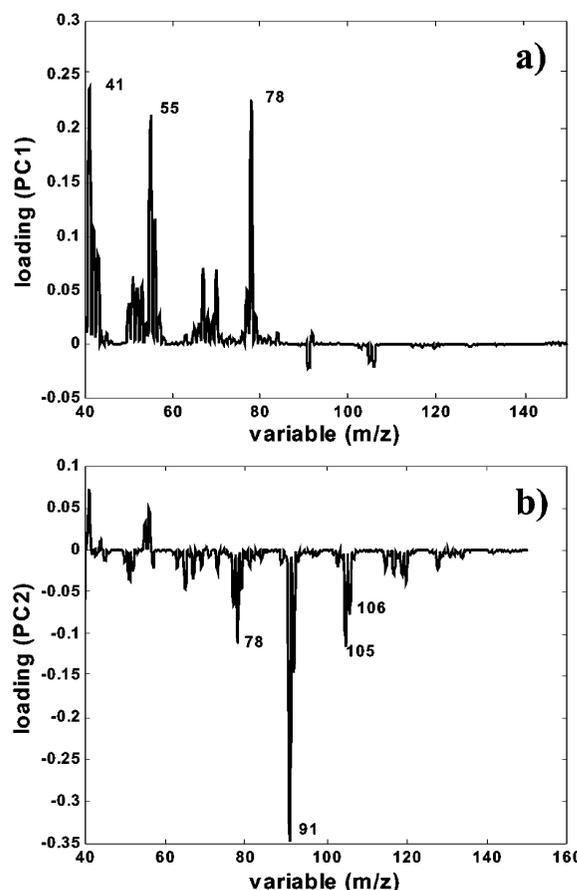


Fig. 7 Loadings for (a) PC1 and (b) PC2 with important variables shown by their m/z ratios.

samples positioned to the right of the vertical line (PC1) are those displaying the m/z 41, 55 and 78 ions of relatively high abundance. Samples positioned to the left of the PC1 line therefore display relatively scarce m/z 41, 55 and 78 ions. PC2 [Fig. 7(b)], which explains ~13% of the data variance, displays the highest loading for m/z 91. Samples displaying m/z 91 ions of relatively high abundance are therefore positioned below the horizontal line (PC2) whereas those displaying scarce m/z 91 ions fall above the PC2 line (Fig. 6).

Conclusions

MIMS has been shown to be efficient for real-time monitoring of the water solubilization of the VOC constituents of gasoline and to evaluate and compare the cosolvent effects of gasoline additives. When using FIA–MIMS, both fast VOC quantitation and mass spectra acquisition can be performed for gasoline-contaminated water samples. FIA–MIMS with chemometric analysis is also able to detect rapidly and efficiently small variances in composition of the water-soluble VOC components of gasoline and the combined application of these techniques is therefore promising for the analysis of gasoline-contaminated water samples. We are currently evaluating its efficacy to identify fuel link sites and fuel adulteration.

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