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Short communication

Identification of potential migrants from a vinylic organosol varnish by gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry

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Abstract

The inner coating of food cans may include epoxy resins, using bisphenol A diglycidyl ether (BADGE) as crosslinking agent. Unreacted BADGE and various derivatives may migrate into foodstuffs. As a prerequisite to migration studies, it is essential to identify all potential migrants in solvent extracts of the coating. In this study the chemical structures of substances extracted from a vinylic organosol are determined by gas and liquid chromatography, coupled to mass spectrometry, on the basis of mass fragmentation patterns and/or comparison with authentic samples. Two classes of substances are found: BADGE, the corresponding monoethers and HCl adducts on one hand, and bisphenol F diglycidyl ether isomers and derivatives on the other hand. The possible origin of these compounds is discussed.

Keywords: Food analysis; Vinylic organosol; Bisphenol A diglycidyl ether; Epoxy resins; Polymers

1. Introduction

The inner coatings of food cans in direct contact with foodstuffs are usually based on epoxyphenolic resins. In vinylic organosol coatings, a second polymer is also used: poly(vinyl chloride) (PVC). The flexible PVC moiety facilitates processing. The polar groups and the tridimensional network of the epoxyphenolic domain, respectively ensure the adhesion of the coating to the metal and its barrier properties. The coating should ideally behave as an inert barrier protecting the metal against corrosion by foodstuffs. However, interaction with food products must be controlled to ensure food quality and/or safety.

The safety assessment of epoxy-based resins relies on their content in low-molecular-mass compounds which may migrate into food, like unreacted monomers [1]. Many of these resins are synthesized from bisphenol A diglycidyl ether (BADGE, CAS No. 1675-54-3, Fig. 1). BADGE is prepared by reacting bisphenol A (BPA, CAS No. 80-05-7) and epichlorhydrin. Bisphenol F diglycidyl ether (BFDGE, CAS No. 2095-03-6, Fig. 1), an analogue of BADGE without methyl substituents, may also be used as

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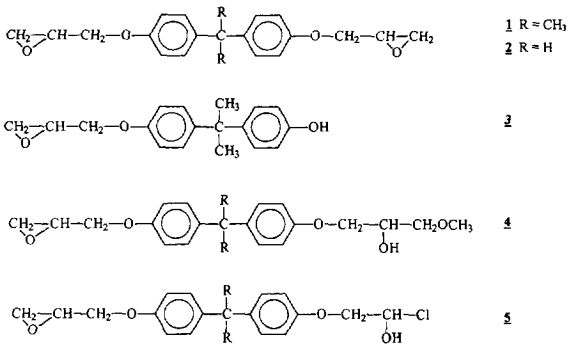

Fig. 1. Structure of BADGE (**1**, R=CH_3), BFDGE (**2**, R=H), BAMGE (**3**), and of the methylolated (**4**) or chlorinated (**5**) derivatives of BADGE or BFDGE.

crosslinking agent. For some time, BADGE has been suspected of being carcinogenic like many epoxy compounds. However studies have shown that BADGE was not mutagenic in vivo [2]. Migration of unreacted BADGE should not exceed 1 mg/kg food [3]. The lowest levels of residual monomers in food packaging material are recommended.

The control of migration from plastics requires as a prerequisite the analytical determination of all potential migrants [4]. For coatings, the starting monomers are highly reactive and it is likely that they are not the real migrants. It is therefore necessary to identify chemicals present in varnish extracts.

As far as epoxy resins are concerned, BADGE and BFDGE, tracked as signatures of contamination by such coatings, have been observed in drinking water by field desorption mass spectrometry of fractions collected from HPLC analysis [5]. Furthermore, impurities and hydrolysis products of BADGE in aqueous solutions have been tentatively identified by liquid chromatography–thermospray mass spectrometry [6]. In contrast and quite surprisingly, to our knowledge, no study has been published using the highly sensitive gas chromatography–mass spectrometry (GC–MS) technique to identify low-molecular-mass BADGE or BFDGE derivatives surviving in vinylic organosol varnish intended to come into direct contact with food.

The objective of this work was to establish satisfactory conditions for the separation and the GC–MS identification of potential migrants of a vinylic organosol (a widely used coating). This will facilitate the migration studies in complex food matrixes or in food simulants. Low-molecular-mass components have been extracted from a cured vinylic organosol varnish and analysed by GC–MS, before and after silylation, using both the electron impact (EI) and the chemical ionisation (CI) methods. To further assess the mass spectral behavior of BADGE and its derivatives, the extracts were also analyzed by liquid chromatography–mass spectrometry (LC–MS), using the electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI) techniques.

2. Experimental

2.1. Samples

BPA, BADGE and BFDGE (kindly provided by Ciba-Geigy) were dissolved in CH_2Cl_2 at a concentration of approximately 1 mg/ml.

The varnish (kindly supplied by Pechiney) was a commercial vinylic organosol product, containing PVC, epoxyphenolic resin and BADGE. After application on a tinned steel plate, it was cured for 20 s at 315°C (normal flash curing conditions) and then separated from the metal plate using mercury [7]. This procedure does not affect the varnish as it is only used to separate the cured varnish from the metal. The recovered sheet of cured varnish was extracted for 3 h with methanol in a Soxhlet apparatus (chromatographic grade, 100 ml). The organic extract was concentrated to 20 ml with a rotating evaporator.

For GC–MS analysis, an aliquot of the methanolic solution was evaporated to dryness and redissolved in CH_2Cl_2.

2.2. Silylation

In a small PTFE-lined screw cap vial, the CH_2Cl_2 extract (20 μl) (previously dried over Na_2SO_4) was reacted with trimethylsilylating reagent (BSTFA, Aldrich, 100 μl) and anhydrous pyridine (20 μl), for 1 h at room temperature.

2.3. GC–MS analysis

Both CH_2Cl_2 and trimethylsilylated (TMS) ex-

tracts and the CH_2Cl_2 BPA, BADGE and BFDGE solutions were analyzed on a DB-5 MS capillary column (J and W, 15 m×0.2 mm I.D., 0.2 μm bonded phase), with helium as the carrier gas (inlet pressure of 0.6 bar). Injections of ca. 2 μl were made by means of a moving needle type injector held at 260°C. The oven temperature was programmed at 2°C min^{-1} from 180 to 280°C. The gas chromatographic system (DI 700, Delsi) was combined with a quadrupole mass spectrometer (Nermag R10-10H), operating in the electron impact ionisation mode. The spectrometer was calibrated with perfluorotributylamine (FC43). The electron multiplier voltage was set at −1.25 kV.The source temperature was set to 100°C. The transfer line to the mass spectrometer was held at 270°C. Mass spectra were recorded at 70 eV (EI), in full scan mode between *m/z* 60 and 600, with a scan time of 1 s.

To confirm mass spectral assignments, GC–MS analysis of the extract and references were operated in the positive and/or negative chemical ionisation mode. The reactant gas was ammoniac (10^{-1} Torr; 1 Torr=133.322 Pa).

2.4. LC–MS analysis

The analysis of the methanolic varnish extract (10 μl analyzed) was performed by HPLC on a Li-Chrospher 5 μm C_8 column (250×4.6 mm I.D., Interchim). An isocratic elution was used with an acetonitrile–water (0.1 *M* ammonium acetate) mixture (50:50, v/v), at a flow-rate of 0.5 ml min^{-1}. The column eluate was split (split ratio 1/10), before entering the mass spectrometer. The mass spectrometer (VG Platforme II, Fisons) was used in the positive mode and by ESI or APCI ionization techniques.

3. Results and discussion

3.1. Choice of extraction solvent

Both isooctane [8] and diethy ether [9] have been suggested to be of general use for screening of plastics food packaging. These solvents as well as methanol and dichloromethane were tried to extract the vinylic organosol coating. Extraction was pursued for 30 min at 40°C with reference to the Dutch official method [9]. Extracts were analysed either directly by HPLC or evaporated, redissolved in C^2HCl_3 and analysed by ^{1}H-NMR. Both techniques gave comparable results. With isooctane, almost no potential migrants were extracted. Although dichloromethane and diethyl ether seemed very efficient, they substantially dissolved resin oligomers which could induce troubles for chromatographic analysis. In contrast, methanol was as efficient for dissolving low-molecular-mass compounds but did not solubilize the resin oligomers. In addition, alcohols are already used for alternative migration test according to European legislation [10]. Methanol was therefore chosen for further experiments. Extraction time and temperature conditions were optimized by UV spectrometry, by monitoring the increase of the maximum at 275 nm, until a plateau was reached.

3.2. GC–MS analysis of BADGE and BFDGE authentic compounds

Since starting substances might survive in the cured varnish, we first examined the GC–MS behavior of BADGE and BFDGE. Their corresponding GC–MS chromatographic and spectral data are reported in Table 1.

Commercial BADGE samples essentially contain BADGE (*m/z* 340), together with three minor impurities accounting for less than 5% of the total amount. On the basis of mass spectral fragmentation patterns, the first eluted impurity peak, with molecular ion *m/z* 284 was assigned to bisphenol A monoglycidyl ether (BAMGE, Fig. 1), resulting from the incomplete condensation of epichlorhydrin on BPA. The two other impurities, with fragments and molecular ions similar to those of BADGE, were tentatively assigned to position isomers, the origin of which may be accounted for as follows. When phenol and acetone are reacted together to prepare BPA, the precursor of BADGE, the *p,p'*-isomer, I.D. BPA, recovered as the major product, may be accompanied with trace amounts of the *p,o'*-and *o,o'*-isomers [11]. During condensation with epichlorhydrin, these isomers of BPA give position isomers of BADGE. Interestingly, no residual BPA, a

Table 1
GC–MS data of the BADGE and BFDGE reference compounds analyzed in the EI mode

Identification	Retention time (min)	Relative surface area (%)	Molecular ion (rel. intensity)	Fragment ions (rel. intensity)
Commercial BADGE preparation				
BAMGE[a]	15.9	0.5	284 (33)	269 (100), 213 (17), 165 (5), 135 (6), 119 (11), 107 (8), 91 (13), 77 (11), 65 (8)
iBADGE[b]	19.1	0.2	340 (100)	325 (60), 269 (14), 211 (14), 205 (19), 191 (17), 175 (17), 165 (17), 145 (17), 135 (14), 131 (17), 119 (19), 107 (38), 91 (40), 77 (26), 65 (19)
iBADGE[b]	24.3	1.8	340 (23)	325 (100), 295 (3), 269 (12), 213 (4), 191 (6), 175 (3), 165 (5), 135 (3), 119 (5), 107 (4), 91 (7), 77 (6)
BADGE	28.3	97.5	340 (29)	325 (100), 295 (2), 269 (5), 213 (3), 191 (3), 165 (3), 135 (2), 119 (5), 107 (3), 91 (5), 77 (4)
Commercial BFDGE preparation				
iBFDGE[c]	15.3	18	312 (8)	235 (17), 223 (12), 221 (11), 219 (10), 197 (34), 181 (100), 165 (10), 152 (19), 141 (7), 131 (14), 119 (13), 115 (15), 107 (26), 91 (18), 77 (12), 65 (5)
iBFDGE[c]	19.6	54	312 (80)	255 (21), 253 (21), 237 (11), 223 (10), 221 (10), 209 (8), 197 (100), 196 (53), 181 (73), 168 (25), 165 (20), 152 (42), 141 (19), 131 (28), 115 (32), 107 (53), 91 (21), 89 (12), 77 (28), 65 (10)
iBFDGE[c]	23.9	28	312 (100)	255 (13), 239 (12), 209 (6), 197 (15), 183 (14), 181 (17), 165 (15), 163 (9), 152 (25), 141 (13), 133 (12), 128 (11), 115 (19), 107 (40), 91 (11), 77 (15)

[a] BAMGE = Bisphenol A monoglycidyl ether.
[b] iBADGE = Positional isomer of BADGE (*p,o′* or *o,o′*).
[c] iBFDGE = Positional isomers of BFDGE (*p,p′*, *p,o′*, or *o,o′*; precise assignment not specified for the *p,p′* genuine BFDGE).

toxic molecule with a very low migration limit [12], could be observed in commercial BADGE.

The mass spectral fragmentation (Table 1) of BADGE, of its position isomers and of BAMGE (**3**) display common features: the most prominent fragment ions result from the loss of the benzylic methyl group ([M−15], base peak for three BADGE derivatives in Table 1). In addition, characteristic ions of epoxy compounds are formed by the loss of the epoxy side chains of the phenolic rings. This fragmentation proceeds through cleavage of the phenolic ether bonds and concomitant hydrogen transfer onto the phenolic oxygen ([M−15−56], at *m/z* 269 for BADGE and 213 for BAMGE; [M−15−2×56] at *m/z* 213 for BADGE). Other ions can be assigned to the fragmentation of BPA, for example typical aromatic ions such as $C_6H_5^+$, $C_7H_7^+$ and $C_7H_7O^+$, at *m/z* 77, 91 and 107, respectively.

When subjected to chemical ionisation with ammonia, BADGE essentially gave rise to the ammonium adduct at $[M+NH_4]^+$, with very weak further fragmentation in the positive mode (base peak at *m/z* 358). In the negative mode, a pseudo-molecular ion $[M-H]^-$ was observed at *m/z* 339 (relative intensity 15%) accompanied with fragment ions at *m/z* 309 (base peak, $[M-H-CH_2O]^-$) and at *m/z* 283 ([M−1−56]; relative intensity 50%). For BADGE, the relative sensitivity of the CI mode

was far lower than that of the EI mode. Accordingly, the minor compounds present in commercial BADGE and observed in the EI total ion current chromatogram (TIC), could not be observed in the CI TIC (data not shown). The CI mode therefore proved to be less efficient than the EI mode for GC–MS analysis of BADGE and its derivatives.

The EI TIC of the BFDGE reference compound showed three peaks with substantial relative intensity (Table 1). The corresponding mass spectra were similar and therefore attributed to position isomers of BFDGE (referred to as iBFDGE in Table 1), without any more precise assignments for lack of appropriate authentic samples. As for BADGE, the spectra of BFDGE isomers showed molecular ions (at m/z 312) of medium to strong intensity, characteristic fragments issued from the loss of one or two epoxy side chains, and unspecific aromatic ions. The main difference between BFDGE and BADGE mass spectra was the absence of fragments resulting from the loss of benzylic methyl groups in the former.

3.3. GC–MS identification of the BADGE and BFDGE derivatives extracted from the varnish

The GC–MS TIC chromatogram (EI mode) of the varnish extract (not derivatized) showed the separation of the low-molecular-mass phenolic compounds remaining in the epoxy-based coating after curing (Fig. 2). The corresponding mass spectral data are reported in Table 2.

The major peak corresponded to BADGE (peak 4, Fig. 2), accompanied with a lower amount of its position isomer (coeluted with iBFDGE in peak 3).

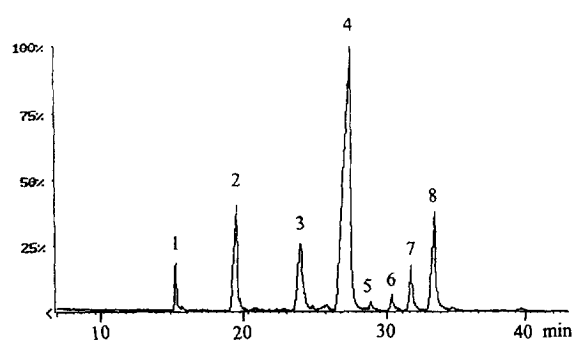

Fig. 2. GC–MS total ion current chromatogram of a varnish extract, obtained in the electron impact ionization mode.

Small amounts of BAMGE were also found. BAMGE was converted to a TMS derivative after silylation of the extract (Table 3). Monoglycidyl ether derivatives of BADGE result from an incomplete reaction of bisphenol A with epichlorhydrin.

The three BFDGE isomers identified in commercial BFDGE were also found in the varnish extract. BFDGE itself is not used as a monomer in common coatings (contrary to BADGE). Its presence may arise from phenol–formaldehyde resins which are commonly used in epoxyphenolic resins. When epichlorhydrine is used as a crosslinking agent, BFDGE and its position isomers could be formed in the coating [13].

No residual BPA could be detected in the varnish extract.

In addition to the compounds present in the reference samples, new derivatives of BFDGE and BADGE could be observed (Fig. 2, peaks 5–8). On the basis of their mass fragmentation patterns (Table 2), peaks 5 and 7 were tentatively assigned to the products resulting from methanolysis of one epoxy ring (structure **4** outlined in Fig. 1). Although reference compounds were not available, this hypothesis, was strongly supported by three points. First, the mass spectra of peaks 5 and 7 showed many fragments common to those of peaks 2 (iBFDGE) and 4 (BADGE), respectively. Second, specific ions observed in the mass spectra of peaks 5 and 7 corresponded to the loss of a $-CH_2-CHOH-CH_2OCH_3$ group. Finally, both peaks 5 and 7 were not present after trimethylsilylation of the varnish extract; instead two new peaks corresponded to their TMS derivatives, at +72 amu confirming the presence of a free hydroxyl group (Table 3). Methanolysis products of BADGE (peak 7) and BFDGE (peak 5) in the varnish resulted from the nucleophilic addition of methanol to the epoxy group. These compounds are not potential migrants as they probably arose during Soxhlet extraction.

Peaks 6 and 8 could be assigned to the products resulting from the cleavage of one epoxy ring of BFDGE and BADGE by hydrogen chloride (structure **5** outlined in Fig. 1). The occurrence of one chlorine atom in these derivatives is clearly evidenced from the relative abundance of the M^+ and $[M+2]^+$ ions, reflecting the natural abundance of ^{35}Cl and ^{37}Cl. Similar to peaks 5 and 7, peaks 6 and

Table 2
GC–MS data of the varnish extract analysed in the EI mode

Peak No.[a]	Identification	Retention time (min)	Relative surface area (%)	Molecular ion (rel. intensity)	Fragment ions (rel. intensity)
1	iBFDGE and BAMGE	15.3	2.6	[b]	[b]
2	iBFDGE	19.6	12	[b]	[b]
3	iBADGE and iBFDGE	23.8	10	[b]	[b]
4	BADGE	27.6	58	[b]	[b]
5	iBFDGE, MeOH[c]	29.0	0.4	344 (100)	256 (23), 255 (19), 213 (21), 199 (30), 197 (35), 181 (28), 165 (20), 163 (25), 152 (19), 12 (19), 107 (51), 91 (10), 89 (49), 77 (10), 75 (10)
6	iBFDGE, HCl [d]	30.5	1.3	350 (39), 348 (100)	312 (12), 255 (15), 239 (18), 213 (11), 199 (35), 197 (28), 183 (31), 181 (29), 165 (24), 163 (32), 152 (24), 133 (12), 119 (12), 107 (82), 91 (19), 77 (28)
7	BADGE, MeOH[c]	31.9	3.9	372 (26)	357 (100), 341 (2), 325 (3), 311 (5), 269 (18), 213 (8), 191 (6), 165 (4), 152 (3), 135 (5), 119 (7), 107 (4), 91 (6), 89 (7), 77 (3), 75 (2)
8	BADGE, HCl[d]	33.6	11.8	378 (8), 376 (22)	363 (37), 361 (100), 340 (2), 325 (9), 305 (2), 269 (6), 252 (1), 213 (9), 191 (12), 165 (4), 152 (3), 135 (5), 119 (9), 107 (5), 91 (7), 77 (5)

[a] Peak numbers refer to quotations in Fig. 2.
[b] See Table 1 for mass spectral data.
[c] Structure outlined in Fig. 1.
[d] Structure outlined in Fig. 1.

Table 3
GC–MS data of the TMS derivatives observed in the silylated varnish extract[a]

Identification	Retention time (min)	Molecular ion (rel. intensity)	Fragment ions (rel. intensity)
BAMGE, TMS	16.0	356	341 (100), 285 (4), 207 (6), 193 (7), 177 (3), 165 (4), 149 (5), 119 (5), 107 (4), 73 (46)
iBFDGE, MeOH TMS	30.3	416 (31)	361 (5), 256 (3), 221 (3), 207 (5), 191 (3), 163 (21), 161 (6), 147 (13), 129 (6), 115 (5), 107 (19), 103 (27), 89 (20), 73 (100)
iBFDGE, HCl TMS	32.3	422 (8), 420 (21)	328 (8), 269 (1), 207 (1), 197 (2), 181 (2), 165 (6), 163 (10), 153 (4), 151 (8), 133 (3), 107 (14), 93 (4), 73 (100)
BADGE MeOH TMS	32.9	444 (4)	429 (2), 399 (6), 341 (2), 326 (19), 311 (6), 269 (1), 252 (35), 207 (20), 191 (8), 177 (2), 161 (1), 135 (3), 103 (4), 89 (3), 73 (100)
BADGE, HCl TMS	35.0	450 (9), 448 (22)	435 (37), 433 (79), 341 (9), 325 (2), 285 (1), 269 (7), 213 (3), 191 (16), 177 (2), 165 (4), 151 (3), 135 (6), 119 (3), 107 (4), 93 (6), 73 (100)

[a] Besides these main monoTMS derivatives, diTMS minor ones could be observed that most likely stemed from the aperture of the two epoxy rings by HCl and/or MeOH.

8 are replaced by two new peaks at +72 amu after silylation of the varnish extract (Table 3). The observation of these chlorinated derivatives, which are not present in the CH_2Cl_2 solutions of reference compounds, could be assigned to reactions with PVC degradation products during curing at high temperature. It is well known that PVC may undergo degradation and give rise to hydrogen chloride [14] susceptible to attacking the epoxy group of BADGE or BFDGE. Interestingly, it was observed that the relative importance of these chlorine derivatives is affected by the curing conditions. These compounds can therefore be considered as potential migrants of the varnish.

3.4. LC–MS analysis of the varnish extract

The varnish extract was analyzed by LC–MS in the positive mode and using the ESI or APCI techniques. The results essentially confirmed the GC–MS identifications.

The main ions observed on the ESI-MS spectra as potential migrants were the adduct ions $[M+NH_4]^+$, $[M+Na]^+$ and $[M+K]^+$, as illustrated on the ESI spectrum of BADGE in Fig. 3. Besides, the mass spectra showed minor ions at higher m/z values, which can be assigned to adduct formation with the solvent (CH_3CN), and some fragment ions common to the EI and ESI spectra, at lower m/z values (e.g., at m/z 191 in the case of BADGE). On the LC–ESI-MS profile (not shown), some other components eluted before BADGE could be observed in spite of a rather low signal-to-noise ratio. These components showed the same ESI fragmentation patterns as BADGE. The m/z values of their adducts ions fitted with their assignments to BFDGE (adducts at m/z 330, 335, 351) and to the methylolated (at +32 amu compared to the parent epoxy compound) or chlorinated (at +36 amu) derivatives of BADGE and BFDGE.

The LC–MS profile of the varnish extract obtained using the APCI ionization showed a somewhat better signal-to-noise ratio than the ESI one (data not shown). The base peaks observed on the mass spectra corresponded to the solvent adduct $[M+H+CH_3CN]^+$ without any detectable adduct with ammonium, sodium or potassium. On this basis,

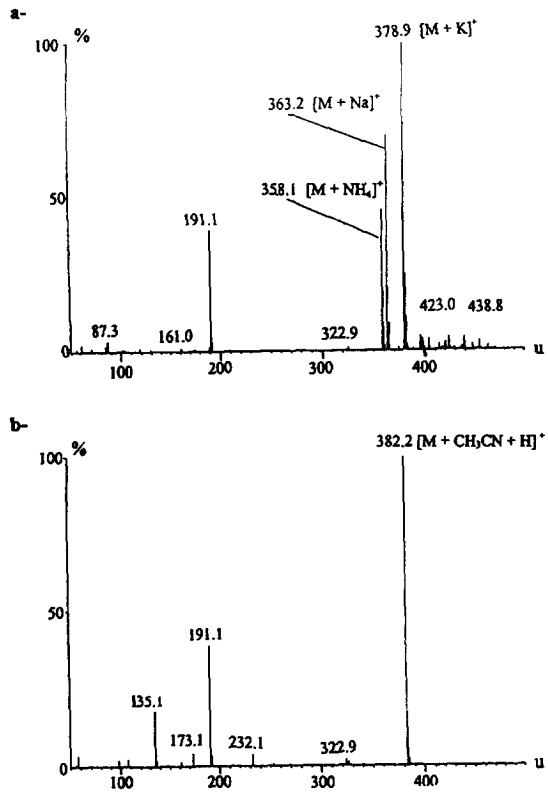

Fig. 3. Mass spectra of BADGE analyzed by LC–ESI-MS (a) and LC–APCI-MS (b).

BADGE (Fig. 3), BFDGE and their methylolated or chlorinated derivatives could be observed as well.

Taken together, the results obtained in LC–MS were in full agreement with the GC–MS identification. However, applied to BADGE derivatives, LC–MS was found to be less efficient than GC–MS, as it produces less informative mass spectra (many adduct ions and few fragment ions).

4. Conclusions

The present study has shown the potential of the highly sensitive GC–MS technique to identify basic features in the mass spectra of potential migrants extracted from vinylic organosols. Two groups of compounds have been recognised: BADGE, BFDGE and their derivatives. LC–MS produced less informative mass spectra than GC–MS but results were similar.

The official approach for plastics has to be adapted for coatings. Besides the starting substances other potential migrants are found in vinylic organosols: they are formed during curing by complex reactions. This approach based on an extraction of the cured varnish rather than on the knowledge of the starting monomers is therefore very useful in studies of coatings.

This investigation will therefore provide the basis to track these potential migrants in food simulants in order to optimize the formulation, the processing and the use of varnishes intended to come into direct contact with food.

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