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Examination of styrene-divinylbenzene ion exchange resins, used in contact with food, for potential migrants

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Abstract

The nature of extractable substances from five types of styrene-divinylbenzene ion exchange resins used in the preparation of foodstuffs was investigated. Strong acid cation resins, strong and weak base anion resins and an active carbon replacement resin were examined. These resins are used for a variety of purposes including water softening, decalcification of sugar syrups, demineralisation, removal of nitrate ions from water and decolourisation. Analysis was carried out using electrospray LC-MS and GC-MS based methodologies. Extractable substances from new resins were identified as mainly being by-products of the resin manufacturing process. Levels of extractable substances decreased with washing.

Keywords: *Ion exchange resin, food contact, styrene-divinyl benzene resin, extractable substances, LC-MS, thermal desorption GC-MS, two-dimensional gas chromatography time of flight mass spectrometry (GCxGC-TOF-MS)*

Introduction

Ion exchange resins are very high surface area materials that have the potential to contaminate food. Annex 1 to EC Regulation No 1935/2004 (EC. 2004), the revised and up-dated food-contact framework regulation, now includes ion exchange resins in the list of groups of materials and articles that may be covered by specific harmonised measures.

A Council of Europe (1997) resolution on ion exchange resins (AP 97/1) includes an inventory list of substances used in the manufacture of ion exchange resins and a migration limit of 1mg/L total organic carbon in the 5th bed volume (water) rinse solution. In the USA, a list of ion exchange resins authorised for food-contact use, together with some restrictions, are given in the FDA regulations Title 21, Section 173.25. A number of successful food contact notifications have been granted for applications of ion exchange resins with specific functionality. Miers (1995) has reviewed US regulations on ion exchange resins. Utsunomiya (1995) has reviewed requirements in Japan.

In this paper we report the chemical nature, extractability and source of potential extractable substances from a range of styrene divinylbenzene ion exchange resins used in contact with food, as received from the manufacturer. No pre-washing of resins as would be recommended before first-use, was undertaken.

Conceptually, ion exchange materials are insoluble acids or bases which, when converted to salts, remain insoluble. Cation exchange materials contain fixed electronegative charges (associated with counter ions), e.g. $\text{RSO}_3^-\text{Na}^+$, and anion exchange materials analogously have fixed electropositive charges, e.g. $\text{RN}^+\text{Me}_3\text{Cl}^-$.

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2
3 Strong-acid cation exchange materials are usually based on sulphonic acids. Strong-
4
5 base anion exchange materials may be quaternary ammonium hydrochlorides and
6
7 weaker base types may be the tertiary amines themselves. Most ion exchange resins
8
9 can be regenerated with appropriate counter ions. It is not uncommon for resin beds to
10
11 be continually used and regenerated over periods of months/years before total resin
12
13 replacement. Some resins are operated at elevated temperatures e.g. 70°C.
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16
17
18 The main applications of ion exchange resins in food processing include the treatment of
19
20 water added to or used with food products, sugar decolourisation/demineralisation,
21
22 isolation of proteins and enzymes from milk products and wine/spirit treatments. Of these
23
24 applications, treatment of water for use with food products is the largest application.
25
26

27
28
29 Potential migrants from ion exchange resins include both organic and inorganic species.
30
31 The latter includes the inorganic ions involved in the process of ion exchange or of resin
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33 regeneration. The type and amount of these will be dependent on the resin types used
34
35 and the manner and sequence of operation. Given the nature of these operations, and
36
37 the copious use of water, it is likely that any problems from ionic impurities will be
38
39 transient ones.
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44 Organic contaminants are potentially more persistent. Organic contaminants in output
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46 streams will include those input contaminants incompletely removed by the resin and
47
48 those contributed by the resin itself. The latter potentially includes: input contaminants
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50 accumulating on the resin and being re-released under breakthrough conditions,
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52 products of thermal or oxidative oxidation of the resin and residues of the chemistry of
53
54 manufacture of the resin.
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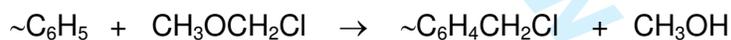
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3 Whilst the first two above are artefacts of the process and the conditions of operation,
4 and are amenable to control in a properly run process, the third is outside the control of
5 the process operators. Studies of water deionisation for the electronics industry (Gottlieb
6 and Meyers, 2000) have found that this third source (residues of manufacture) is the
7 largest source of organic impurities. Such leachable organic impurities are at their
8 highest level in brand-new resins, and gradually rinse out with time.
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18 **Materials and Methods**

19
20 The ion exchange resins examined were suitably functionalised styrene-divinylbenzene
21 resins. Cation exchange styrene-divinylbenzene resins are acid or acid-salt
22 functionalised. For these resins, the initial step is sulphonation of the aromatic ring, e.g.:
23
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25



27
28 Styrene-divinylbenzene anion exchange resins are obtained via chloromethylation. The
29 reaction is complex and may be represented in a number of ways. Conceptually it is a
30 reaction of chloromethyl ether. Chloromethyl ether is created in situ by formaldehyde/HCl
31 reaction.
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40 This is then followed by amination:



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45 Resins were analysed as supplied by the manufacturer.
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3 *Strong acid cation exchange resins*
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5 Two styrene divinyl benzene cation resins with sulphonate functionality (Resins A and B)
6 were analysed. Resin A complied with European standards for use in potable water
7 applications and was in compliance with the U.S. Food and Drug Administration Code of
8 Federal Regulations section 21, paragraph 173.25, for use in the treatment of foods for
9 human consumption. This gel type resin is used for water softening and has ~10%
10 cross-linking. Resin B was a macroporous cation exchange resin. It is used in the
11 decalcification of sugar syrups during isolation of sugar from sugar beet.
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23 *Weak base anion exchanger*
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25 Resin C was a macroporous poly(vinylbenzyl) tertiary amine exchanger of moderate
26 porosity, specially developed for use in the demineralization of juices from the beet, cane
27 and liquid sugar industries.
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33
34 *Strong base anion exchanger*
35

36 Resin D was a macroporous strong base anion resin that is specially designed for the
37 removal of nitrates from water for potable processes. The macroporous matrix and
38 special ion exchange group functionality imparts nitrate selectivity, making this resin
39 particularly suitable for nitrate removal, even when moderate to high concentrations of
40 sulphate are present.
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49 *Macronet resin*
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51 Resin E was a macroporous cross-linked polystyrene based Macronet of very high
52 internal surface area, approaching that of activated carbon. Macronet resins show little
53 or no change in swelling with change of the permeating liquid (Dale et al. 2000). The
54 chemical structure of Resin E was similar to the weak base anion Resin C. However,
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1
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3 many -CH₂- groups link neighbouring aromatic rings (across and within chains), with just
4
5 a few 'unchained' aromatic rings with the functional group attached. Resin E pore
6
7 structure was tailored for the efficient sorption of medium to high molecular weight colour
8
9 bodies such as those found in sugar solutions.
10

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14 Details of the functionality of the resins examined are shown in Figure 1.
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18 The studies undertaken on potential migrants and their extraction behaviour included an
19
20 examination of: volatiles, water-soluble material from the resins, methanol soluble
21
22 organic material and extractables into the EU food simulant 10% ethanol under various
23
24 extraction conditions. The 10% ethanol simulant was considered to be more extractive
25
26 than using distilled water alone and is recommended by the FDA for evaluating ion
27
28 exchange resins used in contact with milk and milk products. A limited examination of
29
30 air-dried aged resins was also undertaken.
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33 34 35 36 **Examination of volatile species**

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38 Volatile species from the resins (0.3g) were analysed using thermal desorption GC-MS.
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40 A Perkin Elmer ATD-400 thermal desorption unit with associated cold-trap was
41
42 employed. The GC-MS instrument was a Perkin Elmer autosystem XL. Desorption
43
44 condition was 20 minutes at 150°C. A Restek RTX-5MS 30m x 0.25mm, 0.25 µm film
45
46 thickness column was used for separation. The column temperature program was 40°C
47
48 for 5 min; 20°C/min to 300°C and held at 300°C for 12 min. Where possible, component
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50 identifications were made by comparing their mass spectra with reference data in the
51
52 NIST V1.5a mass spectral database.
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3 The major volatile component from the resins as received was water. Although largely
4 removed by the cold trap, water presented some problems in the dynamic headspace
5 work.
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10 11 12 **Examination of water and methanol soluble material**

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14 In a preliminary examination of potential migrants, 1g of each resin was immersed in 2
15 ml of purified water (LC-MS grade) or methanol and subjected to 30 min ultrasonic
16 agitation. Water will extract soluble ionic and polar organic species from the resins.
17 Methanol was selected as being a good solvent for low molecular weight non-ionic
18 extractable resin components. Resulting extracts were then examined by LC-MS under
19 conditions developed using the model compounds toluene sulphonic acid and its sodium
20 salt (for cation resins) and benzyl trimethyl ammonium chloride (for anion resins).
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31 The LC-MS instrument used was an Agilent 1100 Series LC/MSD Trap SL. Extractable
32 materials were examined using an Aqua C18 (Phenomenex) 3 μ m 125A^o pore size, 150 x
33 2.00mm column at a column oven temperature of 45^oC. The mobile phase was
34 acetonitrile 5%, 0.1% formic acid 95% at 0.5ml/min and injection volume 5 μ l. Detection
35 was by electrospray ionisation (ESI) +ve and -ve, and UV absorbance 210nm and
36 280nm. ESI drying gas temperature was 350^oC, nebulizer pressure was 40 psi and
37 drying gas flow 10 L/min.
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48 For the examination of the methanol extracts for non-ionic extractables, gradient elution
49 was employed (mobile phase 50% acetonitrile/50% 0.1% formic acid in water to 100%
50 acetonitrile).
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57 **Resin extraction with 10% ethanol**

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3 After obtaining information on the nature of extractable species soluble in water and
4 methanol, further migration testing with the food simulant 10% ethanol was undertaken.
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6 A quantity of each resin (20ml) was placed in a chromatography column and immersed
7
8 in 10% ethanol. The resin/10% ethanol in the column was stored for 24 hours at 40°C.
9
10 The simulant was then drained and retained for analysis. To examine the ease of
11
12 removal of extractable species by washing, each drained resin was successively washed
13
14 four times with 1 bed volume (20ml) of 10% ethanol (at 40°C) and washings retained for
15
16 analysis. The 24-hour extraction period was selected to mimic a foodstuff left in contact
17
18 with the resin for a prolonged period e.g. overnight.
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25 To investigate rate of extraction of species with time, portions of each resin (20g) were
26
27 stored in contact with 40 ml of 10% ethanol at 70°C for up to 13 days. After various time
28
29 periods, aliquots of solution were removed for analysis. The temperature of 70°C was
30
31 selected as being a typical elevated resin use temperature. Additionally, to examine
32
33 possible effects of ageing, portions of each resin (10g) in loosely capped 40ml glass
34
35 vials were heated in an air circulating drying oven at 70°C for 10 days. After the 10 days,
36
37 20ml of 10% ethanol was added and the solutions stored for 24 hours, after which the
38
39 extract solutions were examined for the presence of any new migrants.
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46 *Extract analysis*

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48 Portions of all of the 10% ethanol extract solutions were examined by LC-MS under the
49
50 same conditions as detailed for the water and methanol extracts. Five ml of each test
51
52 solution was also partitioned with 2 ml of dichloromethane. Dichloromethane partition
53
54 extracts of the solutions were examined by GC/GC-TOFMS (5ml of test solution
55
56 partitioned with 2 ml of dichloromethane over 2 min with vigorous shaking). An Agilent
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6890 Gas chromatograph with a LECO Pegasus III GC/GC-TOF/MS instrument was employed. The primary column was a J and W Scientific DB-5, 10m x 0.180mm, 0.18 μ m film thickness. The secondary column was a SGE BPX-50, 2m x 0.10mm, 0.10 μ m film thickness. Split injection (10:1) at 310 $^{\circ}$ C was used with 1 μ l sample injection. The primary oven program was 40 $^{\circ}$ C for 2.5 minutes, 10 $^{\circ}$ C/min to 300 $^{\circ}$ C and held at 300 $^{\circ}$ C for 5 minutes. The secondary oven program was 75 $^{\circ}$ C for 2.5 min, 10 $^{\circ}$ C/min to 335 $^{\circ}$ C and held at 335 $^{\circ}$ C for 5 min. Mass spectra were collected in the range m/z 25-650 at 70 spectra/sec.

Results

Resins A and B

Volatile species

Dynamic thermal desorption in helium (150 $^{\circ}$ C/20 min) generated no significant detectable organic material from either resin A or B.

Water and methanol extractables

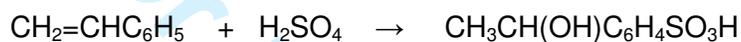
The major ionised species detected in water and their concentrations were similar to those found in the more detailed studies with 10% ethanol. For the methanol extracts, no retained non-ionic species were observed under the gradient elution conditions employed.

10% ethanol extractables

UV Chromatograms for the 10% ethanol extracts for resins A and B after 24 hours contact at 40 $^{\circ}$ C showed similar extractable species with overall levels being lower for Sample B. The UV chromatogram (210nm) for Sample A is shown in Figure 2.

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3 For these resins, the principal extractable components in 10% ethanol, identified from
4 their mass spectra and MS² fragmentations are given in Table 1.
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10 The major extractable component observed CH₃-CH(OH)-C₆H₄-SO₃⁻ (m/z 201) is
11 believed to be the product of sulphuric acid attack on both the ring and the vinyl group in
12 the monomer (styrene) during resin manufacture.
13
14



23 It was more abundant in the extract from the gel resin A than from the macroporous resin
24 B. Other species found include the sulphonated products of ethyl and propylbenzene
25 (ethylbenzene and cumene are anticipated impurities in the monomer). Sulphonation is
26 a very aggressive reaction, and any low molecular weight aromatic components of the
27 original resin are likely to be encountered in their sulphonated forms after
28 functionalisation.
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38 The concentrations of the most abundant extract peak CH₃-CH(OH)-C₆H₄-SO₃⁻ of resin 1
39 and 2 (calculated as sodium p-toluene sulfonate by initial comparison of UV 211nm peak
40 areas) in the different washes are given in Table 2. Levels reduced significantly with
41 washing.
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48 *Aged resins*

49
50 In 13 days contact of resins A and B with 10% ethanol at 70°C, only a small increase in
51 concentration of extractables was observed with storage time. Extractable species
52 detected by LC-MS were as found in the tests at 40°C. No new significant extractable
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3 components were observed. All major peaks showed UV absorption. No extractable
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5 oxidation products were detected in aged dried resin.
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10 Partitioning of the 10% ethanol extracts with dichloromethane gave solutions for more
11
12 detailed GC analysis. In this case, GC/GC analysis was used in conjunction with time-
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14 of-flight mass spectrometry (TOF/MS). By this technique, for resin A, no observable
15
16 differences between the dichloromethane control and the sample dichloromethane
17
18 partition solutions were observed after both 13 days extraction at 70°C or after 10 days
19
20 air ageing at 70°C. No new oxidation or degradation species were observed.
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25 For resin B, with GC/GC-TOF/MS, trace quantities of aromatic species were detected
26
27 after 13 days contact at 70°C with 10% ethanol. Reasonably confident assignments
28
29 could be made to the three most abundant of these, and these are listed in Table 3. It is
30
31 unclear whether these peaks are associated with ageing or slow rate of release from the
32
33 resin. However, amounts detected were all close to the limit of detection of the
34
35 instrumentation.
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37

38 39 40 *Resin C*

41 42 *Volatile substances*

43
44 For resin C, a range of volatile species was detected (Figure 3). In view of the
45
46 compositional complexity of these peaks, no attempts at quantification were made. The
47
48 early peaks were incompletely resolved. Carbon dioxide dominated, providing the peak
49
50 at 1.85 minutes and tailing into the later peaks. Both styrene and chlorostyrene were
51
52 detected at similar levels. The presence of chlorostyrene highlights the complexity of the
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54 chloromethylation reaction during functionalisation of this anionic resin, which involves
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3 electrophilic ring substitution and (commonly) Lewis acid catalysts. Substitution by
4 chlorine becomes a viable side reaction under these conditions.
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10 Other side reactions of chloromethylation include those of the intermediate ArCH_2^+
11 cation, which may itself undergo electrophilic substitution. For example in the case of
12 reaction on low MW aromatics, coupled products of the form ArCH_2Ar are obtained.
13
14 Coupling may well occur here, although the excess or polymer-supported aromatic rings
15 will ensure that the such coupling effectively serves to bind such by-products into the
16 polymer.
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23
24 In the case of styrene, the chloromethylation reaction is potentially polymerising if the
25 ArCH_2^+ cation initiates a vinyl polymerisation. Furthermore, if the cation is ortho to the
26 vinyl group, an internal cyclisation is possible. With elimination of a proton, the two-ring
27 aromatic indene (benzocyclopentadiene, C_9H_8) would be obtained. The trace
28 component at 8.90 min is an aromatic of MW 116. The mass spectrum is shown in
29 Figure 4. This might correspond to either methylphenylacetylene, $\text{CH}_3\text{C}\equiv\text{CC}_6\text{H}_5$, or to
30 indene). A feasible route to the acetylene cannot be formulated, and hence the
31 assignment given here is to indene.
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44 Chlorinated species are particularly easy to recognise by their isomeric distributions.
45 The isotopes ^{35}Cl and ^{37}Cl should be present in the ratio of 3:1. Thus, chlorostyrene
46 has two principal molecular ions (at m/z 138 and 140) in roughly the ratio 3:1. The large
47 peak at 7.26 min has molecular ions in this ratio. They are at m/z 110 and 112 and there
48 is a significant fragment at m/z 75 ($M - \text{Cl}$). The base peak is at m/z 45, which is
49 possibly $\text{CH}_3\text{OCH}_2^+$. In this case, a credible assignment is chloromethyl methyl formal,
50 $\text{CH}_3\text{OCH}_2\text{OCH}_2\text{Cl}$. This is an adduct of HCl and two molecules of formaldehyde. No
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3 reference spectrum was found for this molecule, although the base peak at m/z 45 is
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5 seen in related species chloromethyl derivatives, including chloromethyl ether.
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9
10 Dichloro- species have three principal molecular ions, i.e: M , $M+2$, $M+4$ - in the
11
12 abundance ratios 3:2:1. Thus BCME (bis-chloromethyl ether) would have molecular ions
13
14 at m/z 114, 116 and 118. No BCME was found in resin C.
15
16

17
18 One component, which does show this characteristic dichloro- pattern, is that at 11.82
19
20 min (Figure 5). This shows the 3:2:1 ratio at m/z 213/215/217, which is repeated at m/z
21
22 values 183/185/187, 153/155/156 and 124/126/128. There is also what appears to be a
23
24 monochloro- fragment at m/z 89 and 91 (i.e. loss of Cl from 124/126/128). It is not easy
25
26 to invoke any specific structure here. If the molecular ion pattern is 213/215/217 then
27
28 the initial fragmentation is likely to be the sequential loss of two molecules of
29
30 formaldehyde. Again this appears to be another molecule based on an
31
32 HCl/formaldehyde adduct.
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38 The spectrum for the major peak at 7.89 min gives a reasonable fit for a C4-substituted
39
40 cyclohexane ($C_{10}H_{20}$, MW 140) or dimedone (5,5-dimethyl-1,3-cyclohexadione, $C_8H_{12}O_2$,
41
42 MW 140). What appear to be other cyclohexyl derivatives are seen at 8.18 min and
43
44 10.06 min. Traces of solvents such as tetrachloroethylene (possibly used to swell the
45
46 polymer prior to derivatisation) and decane/undecane (possibly an extender used in cell
47
48 structure development) were found, but the apparent presence of a range of
49
50 cyclohexane derivatives remains a mystery. The solvent composition for the
51
52 chloromethylation and the amination manufacturing steps is unknown. A summary of the
53
54 assignments for the volatiles from resin C is given in Table 4.
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Methanol extractables

Several UV absorbing extractable constituents were detected under the 50% acetonitrile/50% 0.1% formic acid in water to 100% acetonitrile gradient conditions (Figure 6). Fragmentation of the main m/z 220 ion from the peak eluting at the solvent front showed a loss of 45 associated with $\text{NH}(\text{CH}_3)_2$. This loss was also seen in the peak eluting at 1.1 minutes. No ESI response was found for UV absorbing peaks between 1.6 and 4.8 min indicating that they are unlikely to be very polar or ionic in nature.

10% ethanol extractable substances

For resin C, low levels of extractable species were observed by LC-MS, even after 13 days at 70°C (much lower than Resins A and B). No species were detected by LC-MS in the wash solutions. Some extractable components were observed by GCxGC-TOFMS (Figure 7). The largest peak, at 620 sec, gave a mass spectrum identical to that seen at 11.82 min in the resin volatiles (Figure 5). This spectrum shows the spectral features of a dichloro- compound. The assumption made previously was that this was a molecule based on an HCl/formaldehyde adduct. Whilst a precise structure cannot be determined, it is interesting to note that the detection here indicates stability to hydrolysis or ethanolysis. The amount present in the extract was estimated to be at the low mg/kg level.

Ethanolysis of chloroformals would be expected to give rise to structures of the type $\text{EtOCH}_2\text{OCH}_2\text{Cl}$ (MW 124/126). The small peak at 550 sec shows the classic monochloro- isotopic pattern at m/z 124/126 and m/z 154/156, and may well correspond to the component $\text{EtO}(\text{CH}_2\text{O})_2\text{CH}_2\text{Cl}$. No component with a parent ion pairing at 124/126 was seen, although it is interesting to note that the component at 170 sec appears to have the ions at m/z 142 and 144 in the classic monochloro- pattern. Whilst

1
2
3 it is tempting to speculate on whether an increase of 18 Daltons on 124/126 might be
4
5 accountable as stable hydrate, it seems doubtful that such a hydrate would survive the
6
7 gas chromatography.
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9

10 11 *Resin D*

12 13 *Volatiles*

14
15 The chromatogram obtained (Figure 8) shows a number of peaks with the same mass
16
17 spectra. For example, three closely eluting peaks had the mass spectrum of carbon
18
19 dioxide, whilst the peaks from 3.37 min upwards had the mass spectrum of triethylamine.
20
21 Although amine chromatography is not straightforward, it is not clear why such widely
22
23 separated peaks should all analyse as triethylamine. Indeed the similarity amongst the
24
25 spectra for the peaks from 3.37 min upwards was particularly noteworthy. None of the
26
27 spectra showed any ions at higher m/z than for the molecular ions (M , $M+1$ and $M+2$) of
28
29 triethylamine.
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35 It may be significant that ethyl chloride was also found (1.95 and 1.99 min) – hence the
36
37 possibility of some association in the cold trap of the dynamic headspace unit. Any
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39 delay in thermal dissociation raises the prospect of staggered injection, although the
40
41 number of discrete peaks is difficult to rationalise.
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46 47 *Water and methanol extractables*

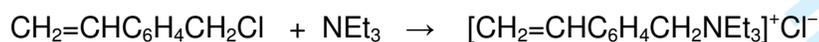
48
49 No significant extractable species were detected in the short-term tests.
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51 52 *10% ethanol*

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54 By LC-MS, no abundant extractable species were detected in the 24 hr 40°C extract
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56 from resin D. On prolonged contact at 70°C, the concentration of extracted species
57
58 increased with contact time. Three main extractable species were detected (Figure 9)
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3 The peak at 0.9 min is characterized by molecular ions at m/z 239 and 241 in
4 abundances characteristic of a monochloro- compound. Fragmentation of the 239 ion,
5
6 produced an ion of mass 102 (loss of 137). This suggests that this peak is an adduct of
7
8 chlorostyrene (mol wt 138/140) with triethylamine (MW 101). By analogy with other
9
10 quaternary ammonium salts, this might be envisaged as the salt $[\text{C}_8\text{H}_7\text{NEt}_3]^+ [\text{Cl}]^-$,
11
12 however, full dissociation is unlikely as the C-Cl bond, when the chlorine is bound to an
13
14 aromatic carbon, is too strong for ionisation. So the adduct is probably better described
15
16 as $[\text{CH}_2=\text{CHC}_6\text{H}_4\text{Cl}][\text{NEt}_3]$ - polar enough to be extracted by the aqueous ethanol, but not
17
18 truly ionic.
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25 The peak at 2.9 min was not chlorinated. The 236.1 ion observed, fragmented into ions
26
27 of m/z 135.0, 100.1, 86.2 (consecutive losses of 101, 35, 14). This suggests that this
28
29 peak could be the hydrated ion of the triethylammonium salt of methylstyrene
30
31 $[\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NEt}_3]^+$ (i.e. the hydrated vinylbenzytriethylammonium ion) with loss of
32
33 triethylamine (m/z 101) giving the m/z 135 fragment. This is the expected by-product of
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35 aminolysis of chloromethylstyrene.
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48 The extractable substance at 6.0 min is also not chlorinated. The parent ion is at m/z
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50 234.2 – i.e. 2 Daltons lower than for the component at 2.9 min. The fragment ions
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52 occurred at m/z 133.0, 100.1 and 86.2 (consecutive losses of 101, 33, 14). The similarity
53
54 with the peak at 2.9 min, coupled with difference of 2 Daltons suggests an ion related to
55
56 vinylbenzytriethylammonium ion but with two hydrogens less. By reference to the earlier
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3 findings on resin C volatiles, this may be an indene derivative. The MW corresponds to
4
5 the hydrated indenyltriethylammonium ion $[\text{C}_9\text{H}_7\text{NEt}_3\cdot\text{H}_2\text{O}]^+$.
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10 These assignments are summarised in Table 5.
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14 By GC/GC-TOF/MS the only main extractable substance detected was ethyl benzoate –
15
16 again a possible product of ethanolysis. An increasing concentration of ethyl benzoate
17
18 with storage time was noted.
19

20 21 22 23 *Resin E*

24 25 *Volatiles*

26
27 Possible traces of acetone were seen at 2.2 min (Figure 10). No other identifications
28
29 were made.
30

31 32 *Water, methanol and 10% ethanol*

33
34 Very little extractable material was observed by LC-MS in the tests at 40°C and 70°C. No
35
36 significant extractable components were detected in the dichloromethane partition
37
38 solutions. No observable differences between the control and the aged sample
39
40 extractions were observed.
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43

44 45 **Conclusions**

46
47
48 Extractable substances from the strong acid cation resins with sulphonate functionality
49
50 (resins A and B) were identified as being reaction products of styrene and/or the resin
51
52 backbone with sulphuric acid during manufacture of the resin. The major extractable
53
54 species was thought to be the product of sulphuric acid attack on both the ring and vinyl
55
56 group on styrene monomer to give a hydroxyethylsulphonic acid, $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_4\text{SO}_3\text{H}$.
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3 Levels of hydroxyethylsulphonic acid were reduced during repeated washing of the
4 resin.
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10 For the weak base anion exchanger (resin C), a wide range of aromatic, aliphatic and
11 chlorinated volatile species were found. Extractable substances into 10% ethanol
12 included several species from the chloromethylation step of the manufacturing process.
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18 For the strong base anion exchanger (resin D), extractable substances included an
19 adduct of chlorostyrene with triethylamine. The expected by-product of aminolysis of
20 chloromethylstyrene was also found as the hydrated vinylbenzyltriethylammonium ion
21 $[\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_2\text{NEt}_3]^+$. Other reaction products of styrene chloromethylation include
22 a possible internal cyclisation to indene or derivatives.
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31 The Macronet resin E showed a particularly low level of extractable substances.
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36 In the ageing tests undertaken, no new products that could be unambiguously assigned
37 to oxidation were detected.
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40 41 42 **Possible implications of the data on food safety** 43 44

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46 With only a few exceptions, the extractable species from the ion exchange resins tested
47 have not been given specific migration limits or allowable daily intakes by the European
48 Food Safety Authority (EFSA). There is also limited information available on their toxicity.
49 Identified species are in general predictable by-products of the manufacturing process.
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53 Although here the extractable species have been studied from non-washed resins as
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3 supplied by the manufacturer, it is evident that continual washing or repeat use of the
4
5 resins with water or foodstuffs will reduce the level of the reported extractable species.
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10 The Council of Europe 1997 Resolution on ion-exchange resins requires levels of total
11
12 organic carbon to be less than 1 mg/kg in the 5th bed volume water rinse, this being
13
14 consistent with Industrial practice for washing resins with four bed volumes of potable
15
16 water after installation or after regeneration. FDA requirements for ion-exchange resins
17
18 (Title 21 Section 173.25) incorporate a larger 20-bed volume rinse wash prior to testing.
19
20 All of the resins tested, as supplied, are understood to meet one or both of these test
21
22 requirements.
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27 In the resin wash tests undertaken at 40°C, data obtained on the 5th bed volume rinse for
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29 resins B-E indicates that migrant levels have been reduced to low µg/kg levels. For resin
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31 A, the major extractable species was determined as 0.4 mg/kg in the 5th wash.
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33 Therefore, data obtained on specific migrants is generally consistent with overall limits
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35 specified by the Council of Europe. Further studies are required to establish whether or
36
37 not any of the identified migrants can be detected in food processed using these types of
38
39 ion exchange resins.
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44 **ACKNOWLEDGEMENT**

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47
48 This study was funded by the UK Food Standards Agency (Project A03042: Substances
49
50 migrating from ion exchange resins). Permission to publish the data is gratefully
51
52 acknowledged.
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REFERENCES

Council of Europe 1997, Resolution AP(97) 1 on Ion exchange and adsorbent resins used in the processing of foodstuffs.

Dale JA et al. 2000. Macronet, the birth and development of a technology, In: Greig JA, editor. Ion Exchange at the Millennium, Proceedings of IEX 2000, Imperial College Press, p261-268

EC. 2004, Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC

Gottlieb MC, Meyers PS. 2000. New advances in the production of ultra low TOC effluents with virgin resins, In: Greig JA, editor. Ion Exchange at the Millennium, Proceedings of IEX 2000, Imperial College Press, p52-60

Miers JA. 1995. Regulation of ion exchange resins for the food, water and beverage industries, Reactive Polymers 24: 99-107

Utsunomiya Y. 1995. Government regulations on the use of ion exchange resins for the processing of potable water, food products and pharmaceuticals in Japan, Reactive Polymers 24: 121-132

Table 1 Principal extractable components Resins A and B

Peak Number	Main MS ions	MS ² Transitions	Assignment
1 (1.2 min)	173.2 369.0	173.2→154.7	HO-C ₆ H ₄ -SO ₃ ⁻ (2M + Na)
2 (1.4 min)	201.1 425	201→156.8, 136.9, 93.0	CH ₃ -CH(OH)-C ₆ H ₄ -SO ₃ ⁻ (2M + Na)
3 (2.0 min)	229.1	229.1→ 198.9	Not identified
4 (2.2 min)	198.2 419.0	198.2 → 188.9	Not identified (2M + Na)
5 (2.3 min)	185.1 392.9	185.1 → 120.9	C ₂ H ₅ -C ₆ H ₄ -SO ₃ ⁻ (2M + Na)
6 (3.3 min)	199.1	199.1 → 134.9	C ₃ H ₇ -C ₆ H ₄ -SO ₃ ⁻
7 (4.7 min)	211.2	211.2 → 182.9, 147	R SO ₃ ⁻

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Table 2 Effect of washing on levels of the main extractable species from resins A and B

Resin Treatment	Concentration of $\text{CH}_3\text{-CH(OH)-C}_6\text{H}_4\text{-SO}_3^-$ (mg/kg)	
	Resin A	Resin B
24 hours at 40°C with 10% ethanol	46.6	6.2
2 nd wash (40°C)	1.8	0.21
3 rd wash (40°C)	1.6	0.03
4 th wash (40°C)	0.6	0.01
5 th wash (40°C)	0.4	0.002

Table 3 Extractable components from Resin B detected by GCxGC-TOFMS

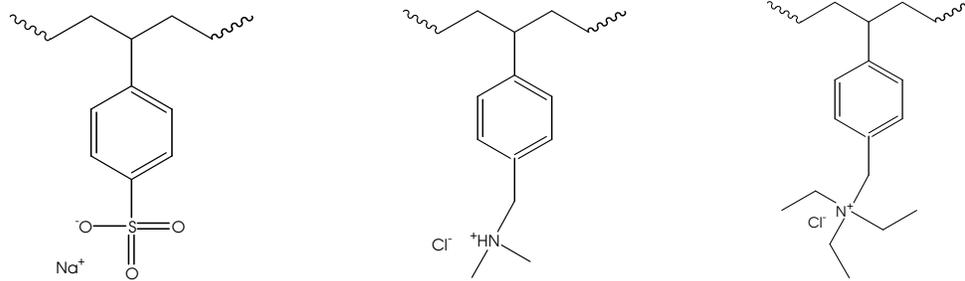
Retention time (sec)	Peak assignment
594.83 , 2.53	butylphenol
899.74 , 2.66	1,1,3-trimethyl-3-phenylindane (alpha-methylstyrene dimer)
1189.64 , 3.75	4,4'-dihydroxydiphenylpropane

Table 4 Volatiles from resin C

Retention Time (min)	Peak Assignment
1.85	carbon dioxide
1.95	methyl chloride
2.10	acetone
6.17	tetrachloroethylene
7.26	chloromethyl methyl formal
7.71	styrene
7.89	C4-substitutedcyclohexane or dimedone (MW 140)
8.18	cyclohexene/cyclohexanone derivative (MW 138)
8.90	indene
9.10	decane
9.73	chlorostyrene
10.06	cyclohexene/cyclohexanone derivative (MW 152)
10.51	undecane
10.67	a methyl ketone
11.82	chlorinated formaldehyde adduct – dichlorinated

Table 5. Extractables from resin D after 7 days in 10% ethanol

Retention time (min)	Peak assignment
0.9	triethylamine-chlorostyrene adduct
2.9	hydrated vinylbenzyltriethylammonium ion $[\text{C}_9\text{H}_9\text{NEt}_3\cdot\text{H}_2\text{O}]^+$
6.0	hydrated indenyltriethylammonium ion $[\text{C}_9\text{H}_7\text{NEt}_3\cdot\text{H}_2\text{O}]^+$



Resins A and B

Resin C

Resin D

Figure 1 Resin Functionality

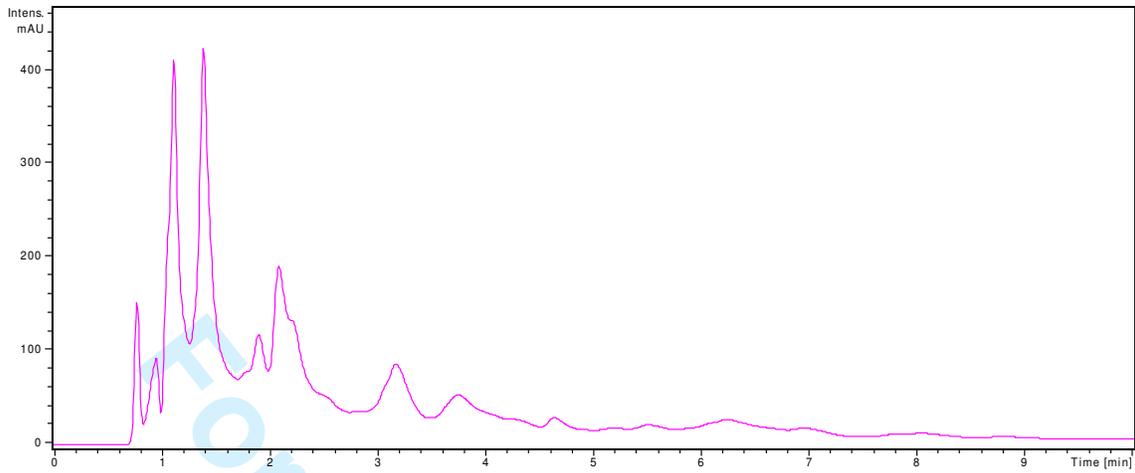


Figure 2 Resin A - UV chromatogram (210nm) of 10% ethanol extract (24 hours at 40°C)

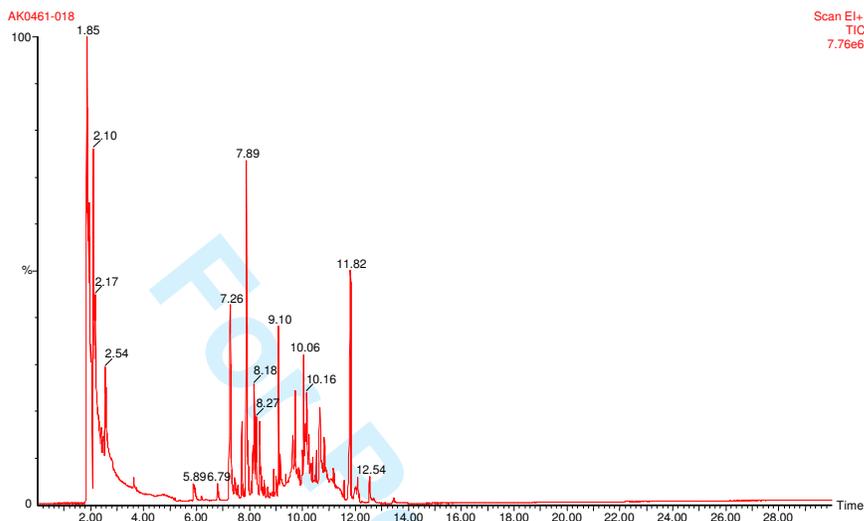


Figure 3 Resin C - Total ion chromatogram of volatiles

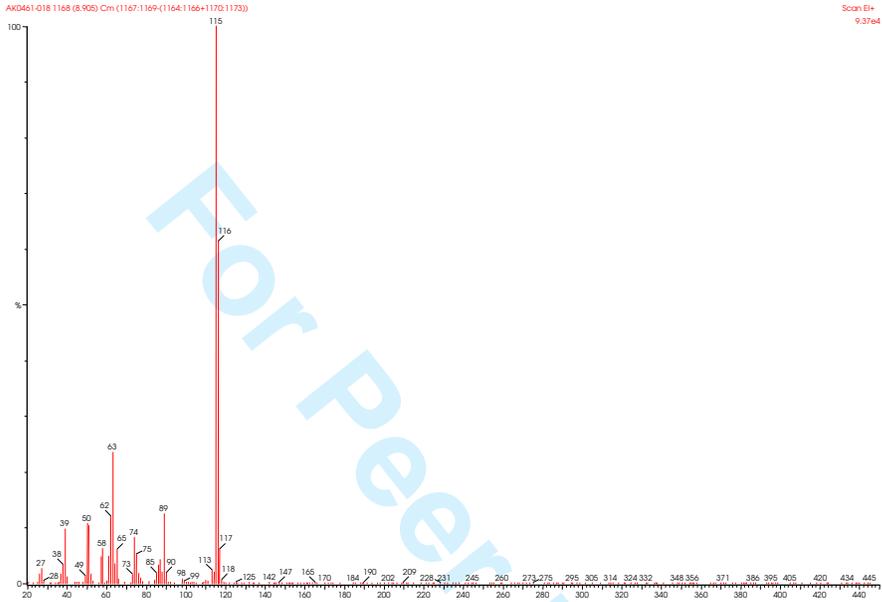


Figure 4 Resin C volatiles - Mass spectrum of small peak at 8.9 min

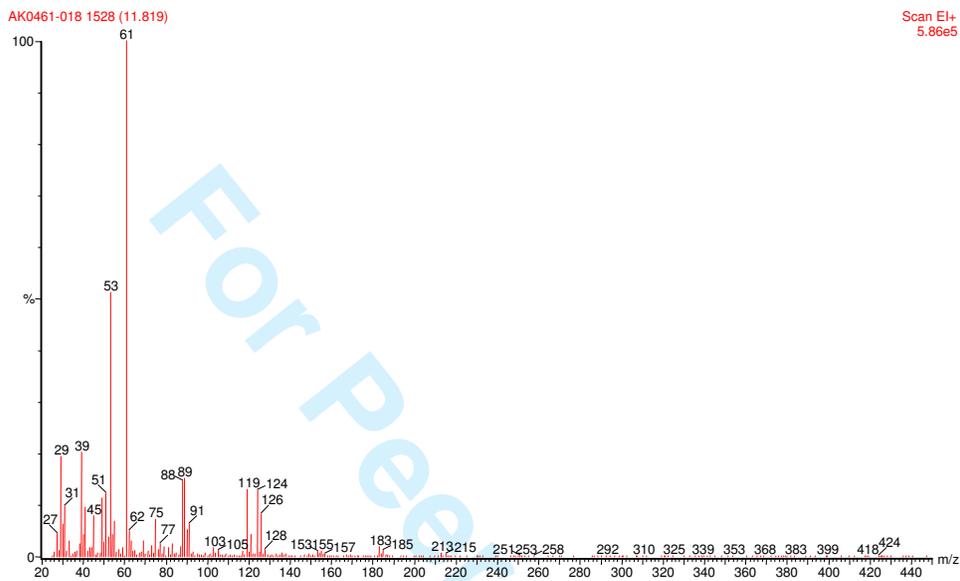


Figure 5 Resin C Volatiles - Mass spectrum of peak at 11.82 min

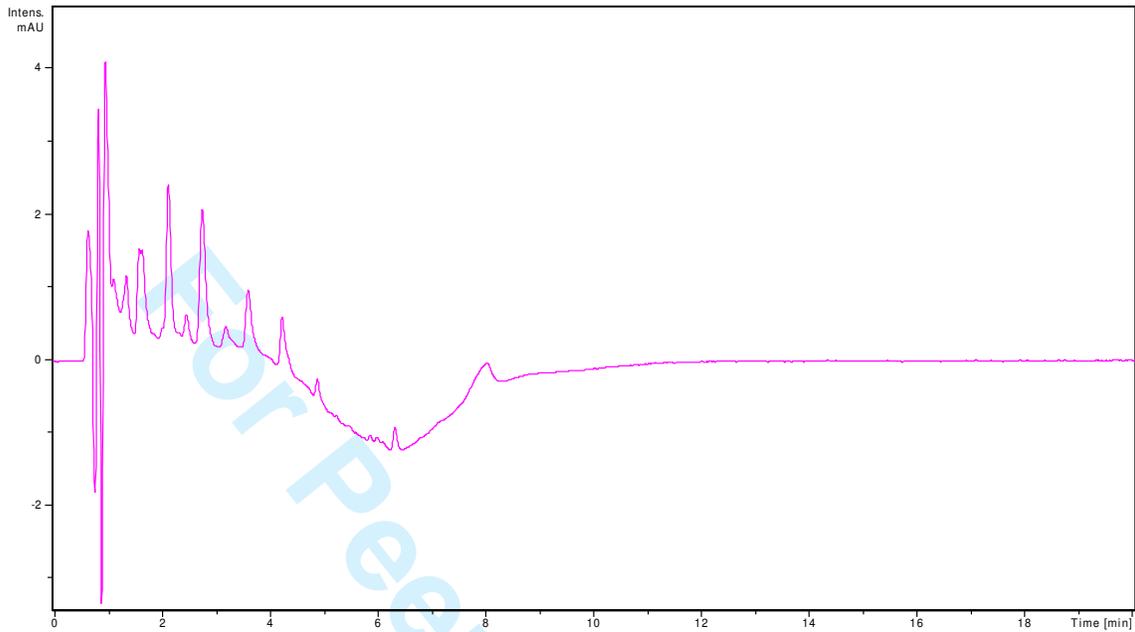


Figure 6 Resin C UV chromatogram (280nm) of methanol extract

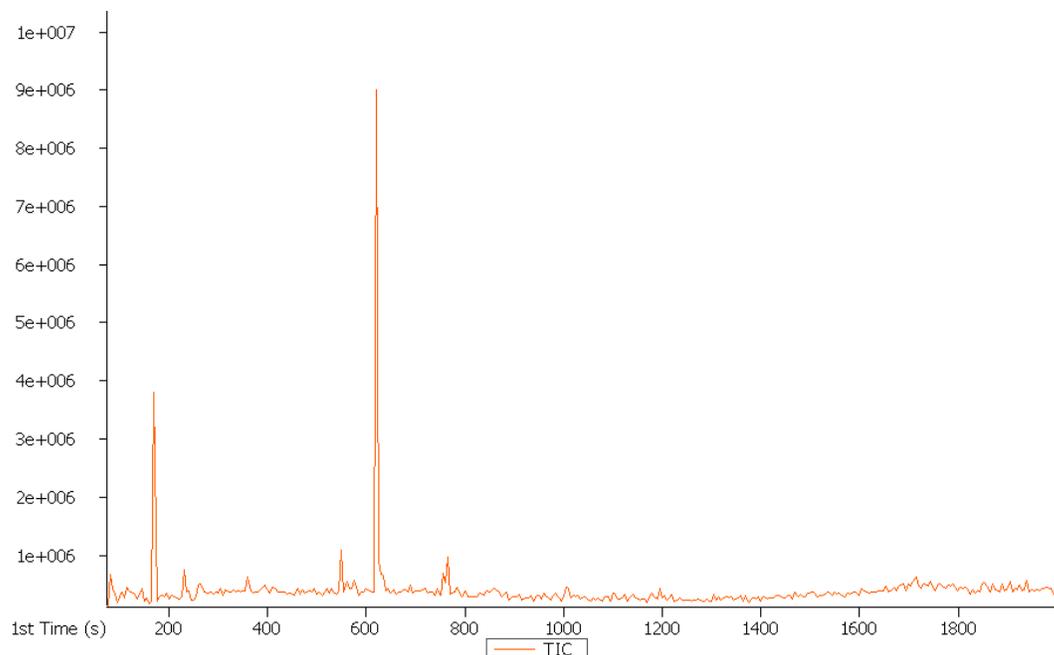


Figure 7 Resin C, reconstructed first dimension total ion chromatogram of the dichloromethane partition solution of 7 day 10% ethanol extraction

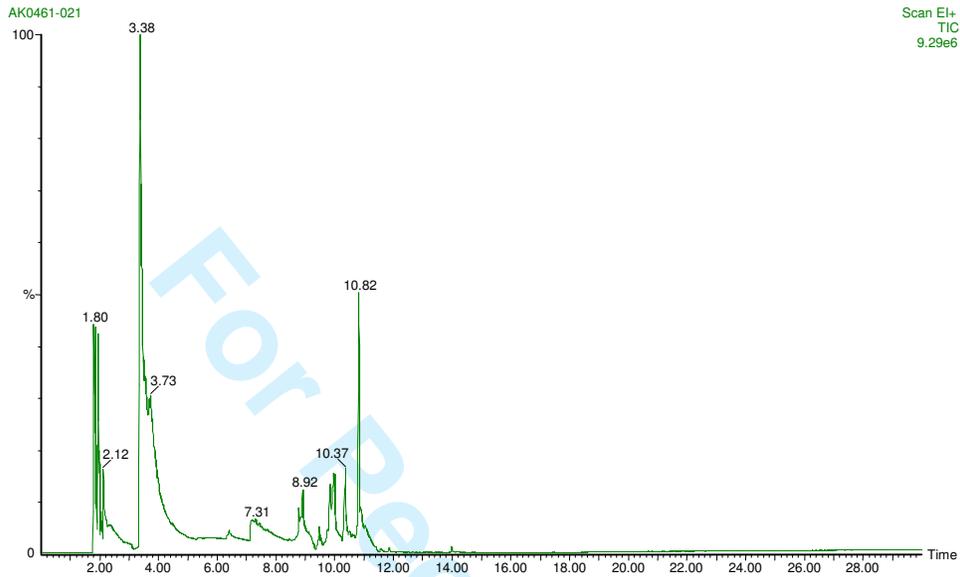


Figure 8. Resin D - Total ion chromatogram of volatiles

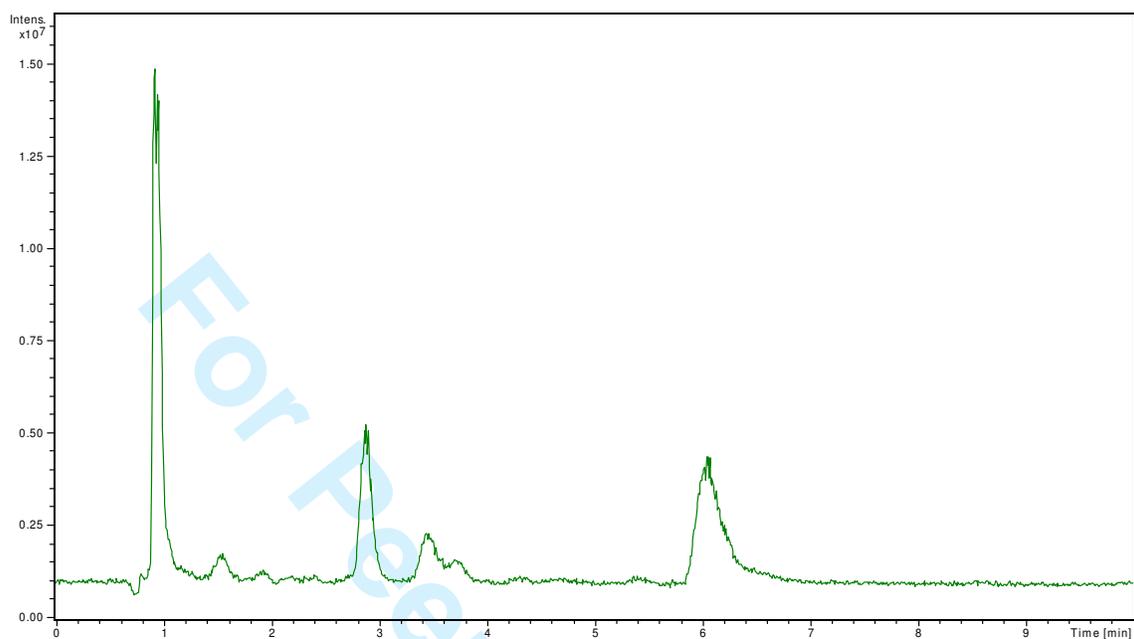


Figure 9 Resin D, +ve APCI chromatogram, 13 days 10% ethanol 70°C extract

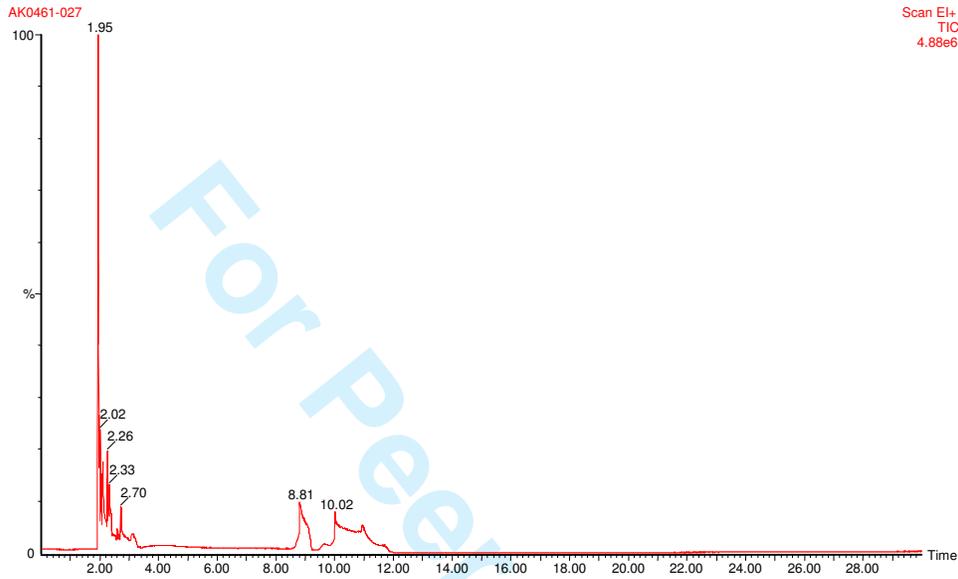


Figure 10 Resin E - Total ion chromatogram of volatiles