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Identification of compounds responsible for an off-odor in wet polyacrylate superabsorbent polymers

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Abstract

Using dynamic headspace, GC–sniff-port coupled to mass spectrometry (MS) and Fourier transform IR [1], and two-dimensional GC–MS–matrix isolation Fourier transform IR [2], we identified the compounds responsible for an off-odor associated with the use of superabsorbent polymers (SAPs) in consumer products. Of those compounds, a C_7 vinyl ketone (5-methylhex-1-en-3-one, isobutyl vinyl ketone) was the best predictor of consumer reaction to the odor. After synthesis, we confirmed this compound as the most offensive odorant in the SAPs. Removing vinyl ketones from the monomer raw material effectively eliminated the product off-odor.

Keywords: Polyacrylate; Polymers; Methylhexenone; Isobutyl vinyl ketone

1. Introduction

Odorous compounds often deliver signals of quality to the foods we eat, to the air we breathe, or to the products we purchase. Interestingly, humans often show exquisite sensitivity and selectivity towards those compounds. For example, we can easily identify, by smell alone, ppb levels of some odorous organic compounds in an air sample that may also contain hundreds of similar compounds. This capability is important to us because knowing the identity of offending odorous compounds often helps to understand and solve odor-related problems. But, matching the human capabilities to identify odorous compounds by the use of analytical instruments poses a difficult challenge.

Because odorous compounds must have some volatility, gas chromatography (GC) coupled with detectors capable of providing molecular information (e.g., mass and IR spectrometers) is often the instrumentation of choice. However, the instruments, used conventionally, produce information with two drawbacks: only ppm-level peaks are identifiable, and the chromatograms may be complex, i.e., may contain a large number of peaks. Circumventing the ppm-sensitivity limitation requires the use of concentration techniques (cryofocusing, solid-phase microextraction, etc.), while dealing with chromatogram complexity can be done by using a human observer as a GC detector (as established by Dravnieks and O'Donnell at the Illinois Institute of Technology in 1971 [3]). By integrating information gathered by the human observer, with information from instrumental detectors, it is possible to focus the identification work on the odor-significant peaks (or chromatographic regions). To facilitate the integration, and to help understand the relative impor-

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tance of odorous chemicals, systems that record odor intensity and odor character, as perceived by the human, have been developed [4]. For those reasons, when we encountered an odor problem with one of our products, we employed a GC equipped with a sniff-port, interfaced to a cryogenic concentrator and mass and IR spectrometers, to locate the regions where odorous compounds associated with the off-odor were eluting.

The problem surfaced as consumers complained about an off-odor in products containing superabsorbent polymers (SAPs). SAPs are partially neutralized crosslinked polyacrylic acids, widely used in disposable diapers and sanitary napkins [5]. Initial work on the problem unequivocally linked the off-odor source to the SAP raw material. Interestingly, solid SAPs were not odorous, but some became highly odorous when wet. This observation suggested the involvement of volatile hydrophobic compounds. Because the odor dissipated over time, we thought there would be a limited reservoir of the offending chemicals, and because the odor of the wet SAP was not pH-dependent, we did not think we had a hydrolysis problem. The approach and instrumentation used to solve the odor problem are the subject of this communication.

2. Experimental

2.1. Materials

SAPs samples were obtained from commercial suppliers or were synthesized in our laboratories. Isovaleric acid, monoglyme (ethylene glycol dimethyl ether) and hydrochloric acid were obtained from Aldrich (Milwaukee, WI, USA). Vinyl lithium was obtained from Organometallics (East Hampstead, NH, USA).

2.2. Equipment

Two chromatographic systems were used in this work. GC–sniff-port was performed on a Hewlett-Packard (HP) Model 5890 Series II GC, equipped with photoionization (PID, OI Analytical Model 5240)–sniff-port, HP 5971 mass-selective (MS), and HP 5965B infrared detection systems. MS and IR signals were processed using the Chemstation software, and PID/sniff-port data were processed by a Perkin-Elmer Nelson system (PE, Turbochrom-3 software) [1]. Proof of identity and matrix-isolated Fourier transform (FT) IR spectra were obtained with a Siemens SiChromat 2-8, two-dimensional (2D) GC system, equipped with an injector/trap and mass and matrix isolation (MI) FT-IR spectrometers 2D-GC–MS–MI-FT-IR [2]. This system allows heart-cutting of a peak as it elutes from one column, and re-analysis in a second column of different polarity. Kovats Retention Indices (*I*) in methyl silicone columns (Restek, Rtx-1) were used to correlate the data obtained in the two systems.

2.3. Collection and analysis of headspace samples

A solid SAP sample (ca. 2 g) was introduced into a 160-ml flask designed to mate with a pre-trap packed with ca. 100–150 mg of Tenax TA. A 5-ml volume of distilled water was introduced into the flask in addition to a PTFE-coated stirring bar. The flask was flushed with helium at 20 ml/min, and a 400-ml sample was collected in the pre-trap while stirring. Collection was done at room temperature.

After collection, excess water was removed by flowing 200–300 ml of dry helium through the pre-trap. The contents of the pre-trap were desorbed at 180°C, while flowing dry helium at 15 ml/min for 8 min, and reconcentrated (at −140°C) in the cryogenic concentrator of the large volume injection (LVI) system [1]. The sample was released from the cryogenic concentrator by heating (to 200°C, at 15°C/s), for analysis. Analysis conditions for GC–MS–PID–sniff-port were as follows: GC: inlet temperature 250°C; oven temperature 50°C for 2 min, then programmed to 280°C at 6°C/min, followed by an isothermal period of 5 min. The column effluent was split ca. 1/10 between the MS and IR/PID systems using an SGE glass-lined splitter. MS: transfer line 280°C; MS temperature 185°C; electron energy 70 eV. Mass range m/z 20–300 (2.5 scans/s) for 20 min, followed by scanning from m/z 30 to 350 (2.2 scans/s) for the remainder of the run. IRD/PID: transfer lines 250°C; light-pipe cell 250°C; source power 21.0 W. IR spectra were obtained by scanning the range 750–4,000 cm^{-1} (1.5 scans/s at

a resolution of 8 cm^{-1}). The effluent from the PID was sent to the sniff-port via a 0.7-mm I.D. glass-lined stainless-steel tube. The temperature of the stainless-steel tube was kept at 180°C by wrapping the tube with glass-coated nichrome wire, and applying power using a specially-designed temperature controller. Analysis conditions for the 2D-GC–MS–MI-FT-IR were as described in [2].

2.4. Sniff-port data recording

The elution time of an odorous compound detected at the sniff-port was established by means of a 10-mV signal delivered by the observer to the Perkin-Elmer Nelson interface. Once an odor was detected, the observer pressed a switch to activate the signal. The delay time between an odor detected at the sniff port and the corresponding peak in the mass or IR spectrometers was typically less than 0.05 min. Odor descriptions were recorded manually. Two observers were used for this study.

3. Results and discussion.

3.1. Identification of key odorants in SAPs

A representative total ion chromatogram (TIC) of a 400-ml headspace sample, collected over wet SAP material, is shown in Fig. 1. The two largest peaks in the chromatogram were identified as 2-propanol and benzaldehyde by their mass spectra and Kovats indices in methylsilicone (I=500 and 943, respectively). Importantly, the two compounds have little odor, and their odor is not similar to the off-odor associated with the SAPs. This is not an uncommon occurrence: large peaks, as measured by instrumental detectors, are often misleading regarding the importance of those compounds to the odor of the sample. For example, two important peaks labeled **A** and **B** in Fig. 1 (I=662 and 725, respectively) are so small as to be readily dismissed by anyone inspecting the chromatogram. Because the identity of large peaks in a chromatogram seldom provides useful information when solving odor-related problems, it is necessary

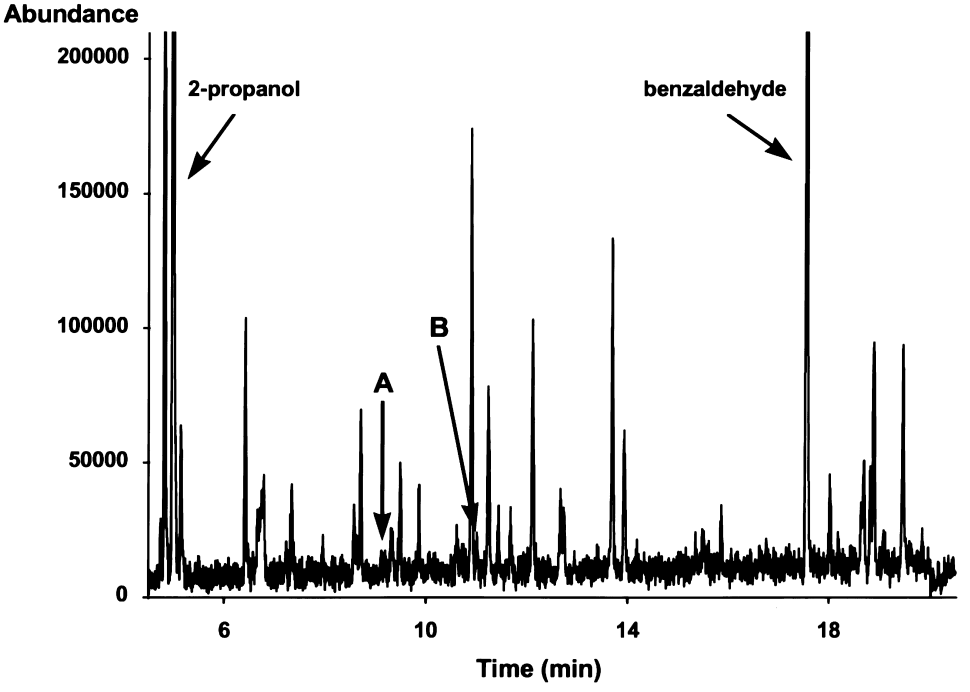

Fig. 1. Total ion chromatogram (TIC) of a 400-ml headspace sample of a wet, odorous SAP.

to focus the identification effort on regions of the chromatogram where odors similar in character to the off-odor occur. To do this it is necessary to use the human as a detector.

To best utilize the human as a detector it is necessary to provide the means to establish the exact time when an odor is perceived, and its place relative to a peak profile. To do that, we generate a signal at the time an odor is detected. While there are many ways to implement the concept, we have chosen to generate a 10-mV signal that can be interpreted by the data system as a peak. Two conditions must be met if one is to relate the time of detection by the human to peaks in the chromatogram: the retention time, and the chromatographic peak profile experienced by the human must be nearly identical to that measured by the instrumental detectors. Those conditions are met by splitting the column effluent so that time differences between the sniff-port and detectors are negligible, and ensuring that the split branches provide adequate transfer of material and inert pathways to the different detectors. If those conditions are met, the time of detection by humans would approach the retention time established by processing the signal from an instrumental detector. By overlaying the two signals, one generated by the human and the other from an instrumental detector, it is possible to establish the exact position in a chromatogram where important odorants elute.

A summary of the regions where odors were detected, and descriptors used by two observers, is shown in Table 1. Note the agreement between Kovats Indices (I) and descriptors in the highlighted text. For example, odor No. 4 was described by the observers as ''plastic, very similar to smell, low intensity'' and ''very much like malodor, weak''. The detection time, expressed as a Kovats index ($I=662$), was the same for both observers. In

Table 1
Odor descriptions of the key odorous compounds in a 400-ml headspace sample of the bad SAP

Odor No.	Odor description (observer 1)	Kovats index	Odor no.	Odor description (observer 2)	Kovats index
			1	Burnt	454
1	**Something, very faint**	**571**	**2**	**Brown, odor similar to malodor**	**571**
			3	Acetic acid, late on button	584
2	Something, very faint	614			
3	Is it background?	633			
4	**Plastic-like, very similar to smell, low**	**662**	**4**	**Very much like malodor, weak**	**662**
			5	Sour odor	670
			6	Weak but similar to malodor	679
5	Late by 1 sec., not sure how to describe, faint	689			
			7	Hot	694
6	**Very much like sample, med.**	**725**	**8**	**Very similar to malodor, med. to strong**	**725**
			9	Very similar to malodor, weak	745
7	**Plastic, very much like sample, med.**	**755**	**10**	**Solvent with malodor, med.**	**755**
			11	Solvent with malodor, med.	756
8	Something, very faint	789			
9	Very quick, very faint plastic	799			
10	Plastic, low	807	12	Plastic, strong	806
11	**Plastic, bad, like sample, med.++**	**808**	**13**	**Plastic, malodor-like, stronger than #12**	**809**
12	Still here, med.	811			
13	Still here, plastic, low	817			
			14	Brown, very weak	851
14	Something, very faint	858			
			15	Strange, sour?, A little late (~2 s), med.	874
15	**Bad, plastic, like sample, med.++**	**918**	**16**	**Similar to malodor, very weak**	**919**
16	Something, very faint	942			
17	Benzaldehyde, low	943	17	Benzaldehyde	943
18	Spray starch, ozoney, low to faint	959	18	Cannot describe	959

general, we expect agreement to ±1 index unit (±0.03 min) for different observers. This is a remarkable agreement considering uncertainties that depend on the chromatography, as well as differences in odor detection, and reaction and processing time of the human observers. Furthermore, agreement between descriptors used by different observers is expected if the compounds are indeed likely to be associated with the offending odor, e.g., $I=725$, odor No. 6 from observer No. 1 and No. 8 from observer No. 2, ''very much like sample, medium intensity'' and ''very similar to malodor, medium to strong intensity'', respectively.

The descriptors and odor intensity data in Table 1 served to focus the identification effort on four odorous compounds eluting at $I=571$, 662, 725 and 806–809. A portion of the chromatogram shown in Fig. 1, is shown in Fig. 2. The upper chromatogram is the total ion chromatogram, while the lower chromatogram represents a selected ion (m/z 55) of the TIC. Note that the Kovats indices of the four odors described in Table 1 correspond to the two small peaks labeled **A** ($I=662$) and **B** ($I=725$) in Fig. 1, and two larger peaks showing a fragment at m/z 55 ($I=571$ and 808). All four peaks have odors similar to the offending odor.

The peak at $I=571$ was identified as 3-butene-2-one (methyl vinyl ketone) based on its mass spectrum and chromatographic retention. This compound has two prominent ions at m/z 55 and 70. The ion at m/z 55 is the base peak of the spectrum, suggesting a stable ion with an acylium-like structure:

$$CH_2=CH-C\equiv O+$$

This ion would be characteristic of compounds containing vinyl ketone-like structures.

The odor detected at $I=806$-809 is associated with a relatively large peak at ca. 13.8 min in Figs. 1 and 2. The mass spectrum, shown in Fig. 3, shows a likely molecular ion at m/z 112, and the characteristic signature ions of a vinyl ketone, e.g., m/z 55 and 70. Those ions and fragmentation pattern are congruent with the structure of a C_7-vinyl ketone. A matrix isolation FTIR spectrum, obtained after cutting the peak to a polar column to ensure that the

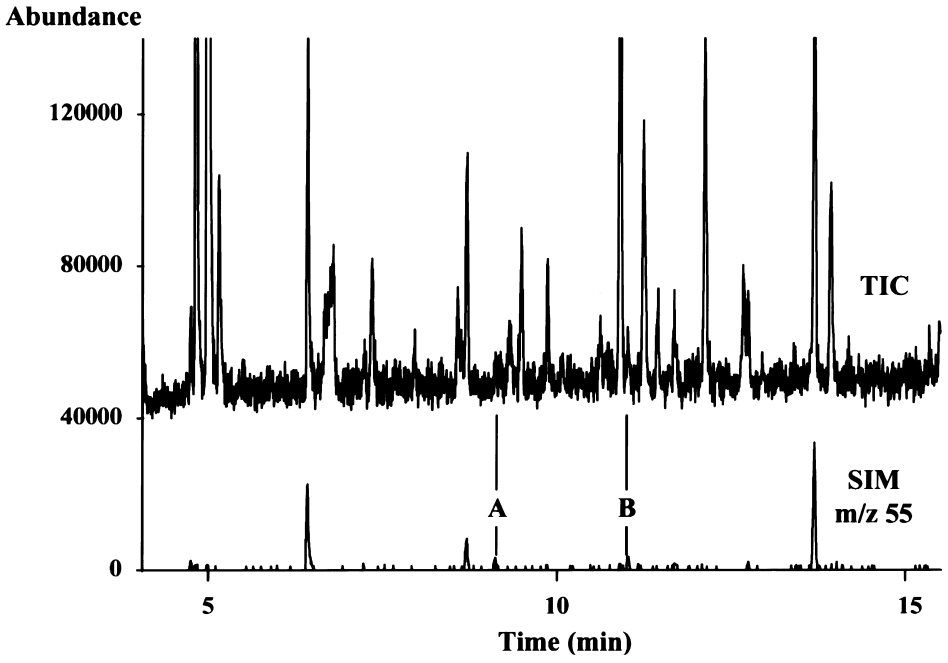

Fig. 2. A portion of the TIC shown in Fig. 1 (upper trace), and the corresponding selected ion chromatogram of the fragment at m/z 55 (lower trace).

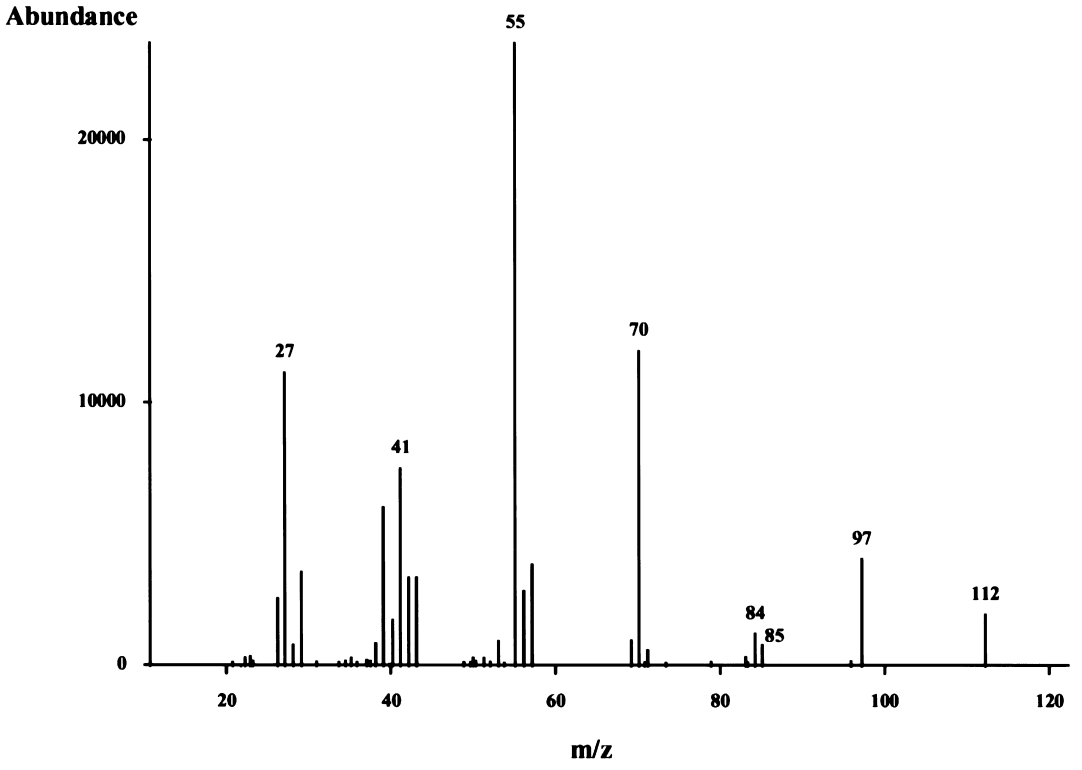

Fig. 3. Mass spectrum of a highly odorous compound detected at *I* 806–809, 5-methylhex-1-en-3-one.

odor was associated with the peak, and not with a compound coeluting with it in the non polar column, is shown in Fig. 4. The characteristic functional group absorptions, i.e., C–C stretches (2968–2883cm^{-1}), C=O stretch (1715,1697 cm^{-1}), C=C stretch (1619 cm^{-1}), C–H bend (1471 cm^{-1}), isobutyl C–H bend (1400–1335 cm^{-1}), were used to suggest [6] isobutyl vinyl ketone (iBVK, 5-methylhex-1-en-3-one) as the structure for the C_7-vinyl ketone.

The range of retention indices for this compound, ca. 3, is larger than the typical error we would expect, i.e., ±1. The range suggests that either there are other odorous compounds coeluting within the peak, or that observers begin to smell the compound at a low concentration, i.e., in the early portion of the peak profile. If true, the compound would have a very low odor detection threshold (ODT), and its removal from the SAPs would be an important step in improving the product. Because the chromatogram in the second dimension revealed no new odorous peaks, we concluded that the C_7-vinyl ketone was a key odorant in the sample. To prove structure and validate our assessment of its importance to the odor problem, we synthesized the compound.

3.2. Synthesis of 5-methylhex-1-en-3-one

Synthesis of the proposed structure for the C_7 ketone, i.e., 5-methylhex-1-en-3-one, was done by reacting isovaleric acid and vinyl lithium using 1, 2-dimethoxyethane as solvent [7]. The synthetic yield was 13%, and the compound had the same odor character perceived in the SAPs with odor problems. The synthesized material was characterized by MS, ^{1}H-NMR and ^{13}C-NMR. ^{1}H-NMR in $C^{2}HCl_3$ revealed resonances for (3H-m) 5.8 ppm, (2H-d) 2.2 ppm, (1H-m) 1.9 ppm, (6H-d) 0.62 ppm, while ^{13}C-NMR showed resonances at 200.49, 136.87, 127.58, 48.5, 42.9, 25.4, 24.8, 22.5 and 22.2 ppm. The retention time on two columns, MS fragmentation and IR spectrum of the synthesized 5-

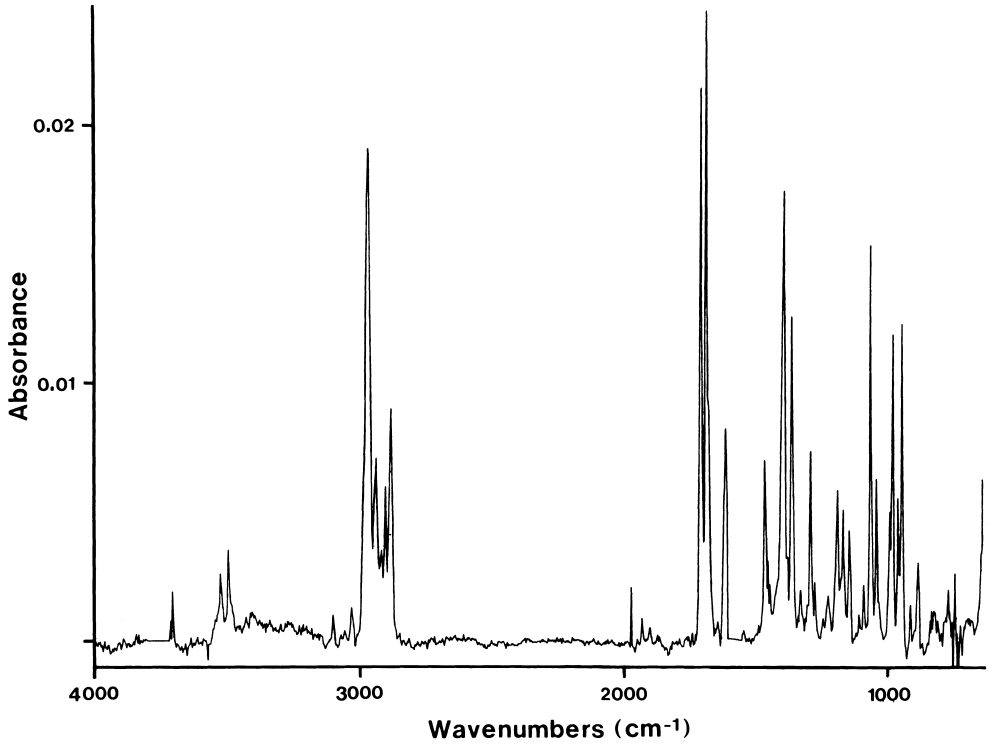

Fig. 4. Matrix isolation FT-IR spectrum of a highly odorous compound detected at *I* 806–809, 5-methylhex-1-en-3-one.

methylhex-1-en-3-one were virtually identical to the unknown C_7-vinyl ketone. The low ODT of this compound, i.e., $<<1$ ppb, confirmed its importance to the problem.

3.3. Solution to the problem

Working with manufacturers of SAPs to remove vinyl ketones, and especially the iBVK, from the monomers used to prepare the polymers resulted in improved materials with little odor. The chromatographic profiles of a bad sample (A) and a sample judged to have no odor problem, (B), are shown in Fig. 5. The chromatograms are similar, although there are a few obvious differences, e.g., large peak at ca. 7.2 min in B. However, the peak areas of the compounds deemed to be key to the odor problem are different, specially in the case of the iBVK where the difference is ca. 50-fold, as indicated by the arrows at 13.8 min in the Figure. This observation confirms our hypothesis of the importance of iBVK to the odor of the sample. Because of its abundance in the bad sample iBVK should be relatively easy to monitor, and thus serve as a marker for efforts aimed at optimizing the SAP manufacturing process. Note that process conditions designed to minimize vinyl ketones in the monomer feedstock also produced reductions in the three other peaks we had associated with the problem, i.e., Kovats 571, 662 and 725, as indicated by the arrows in Fig. 5.

Finally, although we had identity for two materials, $I=571$ and 808, the peaks at $I=662$ and 725, described as having odors similar to the sample, did not yield sufficient mass for identification. However, because both show the ion at m/z 55 as shown in Fig. 2, we believe those compounds are also vinyl ketone-like chemicals. We also estimate the mass of those compounds at less than 1 ng in the 400-ml headspace sample. Thus, their concentration in the headspace is estimated at less than 0.25 ppb. Because of their low concentration in headspace, and because we expect them to have comparable ODTs to iBVK since they likely belong to the same chemical family,

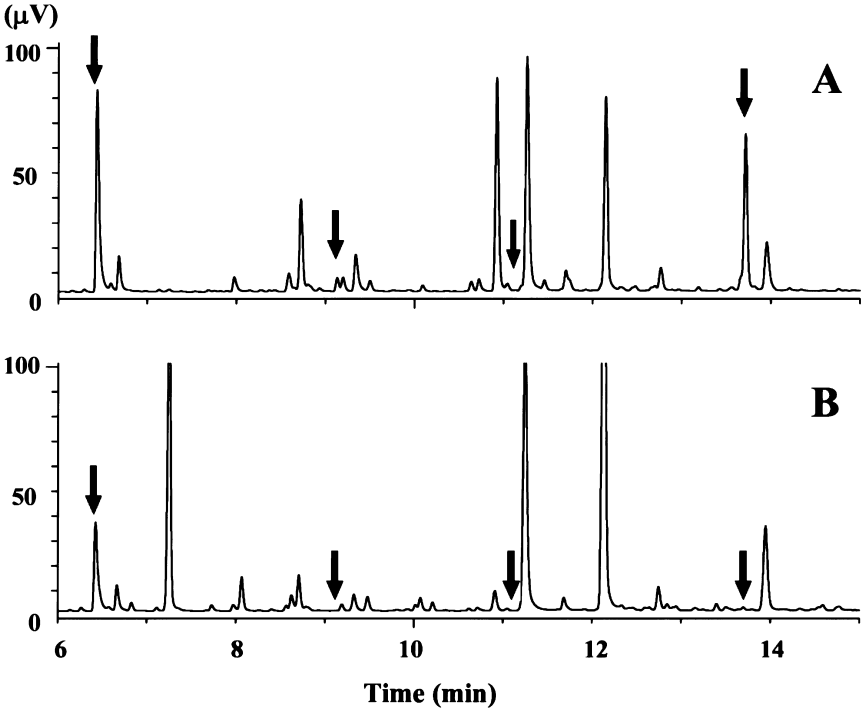

Fig. 5. PID chromatograms of a 400-ml headspace sample of a bad SAP (A), and an improved, odorless SAP (B).

we believe those compounds are likely to have a smaller impact on the sample odor than iBVK.

4. Conclusions

The off-odor of wet SAPs is caused by the presence of compounds with a vinyl ketone-like structure, especially, 5-methylhex-1-en-3-one or iBVK. The identity of iBVK, and its importance to the odor problem, were suggested by GC–sniff-port coupled to mass and IR spectrometers. Its identity and importance were confirmed after synthesis of the authentic compound, and after sensory and chromatographic evaluations of SAPs.

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