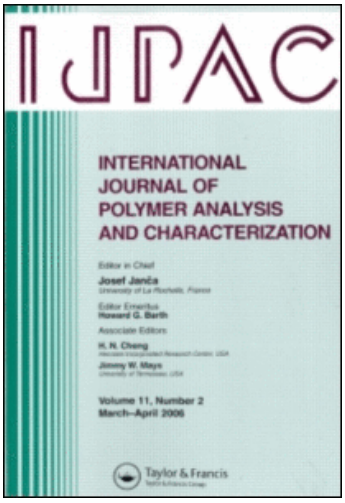

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Mario Lugli[a]; Daniele Becchi[a]; Luca Resta[a]; Leo M. Saija[a]
[a] Cray Valley Italia Srl, Boretto, Italy

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Full-Evaporation Head-Space Gas Chromatographic Technique for the Determination of Residual Monomers and Volatile Organic Compounds in Polymer Dispersions

Mario Lugli, Daniele Becchi, Luca Resta, and Leo M. Saija

Cray Valley Italia Srl, Boretto, Italy

Full-evaporation head-space gas chromatography is a useful technique for the determination of free monomers and other volatile molecules contained in polymer dispersions. The method has a large working range and good repeatability. The absence of contamination in the syringe and the injection line makes it applicable in gas chromatographs equipped with autosamplers. A detailed description of the method and a comparison with the ''traditional'' head-space gas chromatographic technique and the liquid-injection technique described in ASTM D 4827-93 are presented.

Keywords: Gas chromatography; Polymer latex; Residual monomers; VOC

Water-based acrylic and vinyl polymer lattices obtained with emulsion polymerization often contain variable amounts of low-molecular-weight organic compounds, like residual monomers, by-products of cross-linking reactions, initiator-decomposition, and impurities associated with raw materials. The availability of a reproducible and easy-to-use analytical method for the identification and quantitative determination of such

Received 18 December 2000; accepted 25 January 2002.
Address correspondence to Leo M. Saija, Cray Valley Italia Srl, Via Finghè, 42022 Boretto (RE), Italy. E-mail: leo-mario.saija@crayvalley.com

components is of great interest for process understanding, optimization, and quality control purposes. Many analytical gas chromatographic (GC) methods can be found in the literature[1–6]; among them one of the most versatile is the ASTM D 4827-93 test[7] method. This method allows the determination of common low-molecular-weight molecules present in polymer lattices with a single GC run. The analysis is carried out via liquid injection directly from latex samples without any solvent addition. The need for frequent instrument cleaning operations due to polymer deposition in the injection liner and the difficulty of automation are its main disadvantages.

An alternative to the direct injection of a latex sample into the GC column is the head-space technique (HS). Several grams of polymer latex are heated in a vial at fixed time/temperature conditions, and a portion of the gas mixture so formed in the vial is then injected into the GC by a transfer line or a gas syringe. The presence of a polymer phase in the matrix unfortunately generates the following equilibrium, where A is the solute to be determined:

$$A_{\text{polymer phase}} \rightleftharpoons A_{\text{aqueous phase}} \rightleftharpoons A_{\text{gas phase}}$$

As a consequence of this equilibrium, the analyte concentration in the HS-GC determination depends on the type of polymer matrix and its concentration[8,9]. Therefore, the application of this technique to a large number of components contained in different products is not easy because of the need of a correlation curve for each of them.

An improvement of the head-space technique can be accomplished by working at full evaporation conditions. Due to the small amount of sample introduced into the vial, the heating phase causes its complete evaporation, eliminating the above solid-liquid-vapor equilibrium. In this way, it is possible to perform a repeatable evaporation process, independent of the polymer matrix nature. The aim of this work is to compare the ASTM D 4827-93 test method and a full-evaporation head-space GC (FEHS) method for the determination of volatile organic compounds in acrylic and vinyl polymer dispersions characterized by various chemical compositions and volatile organic compounds (VOC) concentration.

EXPERIMENTAL

Reagents

The following analytical-grade chemicals were used: *i*-butanol, hydroquinone monomethyl ether, methanol, ethanol, *i*-propanol, acetone, *n*-butanol, acetic acid, toluene, *n*-butyl acetate, ethyl acetate, methyl acetate (all from Carlo Erba Antibioticos); acetaldehyde, benzaldehyde,

2-ethyl hexanol, *t*-butyl acetate, ethyl benzene, *n*-butyl propionate, 2-hydroxy propyl methacrylate, ethyl methacrylate, *i*-butyl methacrylate, *t*-butanol, acrylonitrile, vinyl acetate, butyldiglycol acetate (all from Fluka); ethyl acrylate, methyl methacrylate, *n*-butyl acrylate, *n*-butyl methacrylate, 2-ethyl hexyl acrylate, styrene, methacrylic acid (all from Atofina); deionized water.

Polymer Latex Samples

The analysis was carried out using 100 polymer latex samples having different monomer composition and conversion degrees, selected from the standard and experimental products of Cray Valley Italia. The concentration range of each unreacted monomer in the latex samples was between 50 and 25,000 ppm. A volatile-free styrene-acrylic polymer matrix was used to prepare reference lattices containing standard amounts of the following monomers: acrylonitrile (AN), vinyl acetate (VAM), *n*-butyl acrylate (BA), ethyl acrylate (EA), methyl methacrylate (MMA), and styrene (STY). Two series of samples characterized by 500 and 1000 ppm of each monomer were prepared.

Samples Preparation

All latex samples were diluted to a solid content of about 8%, using an aqueous solution of *i*-butanol as an internal standard and hydroquinone monomethyl ether (MEHQ) as a polymerization inhibitor. The final concentration of the two substances in each sample was around 300–500 ppm for *i*-butanol and 100–150 ppm for MEHQ.

A double series of samples diluted respectively with water and 50/50 water-methanol solution was also prepared in order to investigate the methanol extraction power with respect to components present within latex particles, as described in ASTM D 4827-93[7].

Gas Chromatographic Analysis

All determinations were carried out on a Fisons GC 8130 equipped with a flame-ionization detector (FID) and a head-space autosampler, CE Instruments HS 500. The autosampler allows the transfer of head-space vapors from the vial to the GC injector through a heated gas syringe to avoid any condensation or absorption phenomena. All separations were performed on a fused-silica capillary column of 60 μm length, 0.53 mm internal diameter, and 3 μm thick cooling of Vocol® stationary phase from Supelco. The separation conditions are summarized in Table I. A typical chromatogram of all chemicals is reported in Figure 1.

TABLE I Gas chromatographic separation conditions

Carrier:	He	5.1 mL/min (40°C)
Head pressure:	50 kPa	
Injector:	170°C	Splitting ratio 5/1-3/1
Detector:	FID; 230°C	
Oven:	40.0°C	for 5 min
	3.2°C/min	up to 85.0°C
	85.0°C	for 0 min
	0.6°C/min	up to 100.0°C
	100.0°C	for 0 min
	15.0°C/min	up to 220.0°C
	220.0°C	for 12 min

For liquid injections, 0.5 μL of prepared samples were introduced into the column by means of a syringe (Hamilton, model 7101). For FEHS injections, 5 μL of prepared samples were introduced by means of a Gilson Pipetman P20 in a 10 mL vial and heated for 150 s at 120°C in the autosampler oven. Then through the autosampler-heated syringe, 700 μL of the gas phase formed in the vial was directly injected into the column.

RESULTS AND DISCUSSION

Dilution Solvent

The influence of cosolvent utilization as a dilution system was investigated by liquid injection of two series of samples diluted respectively with water and with a 50/50 methanol/water solution. As evidenced in Table II, the concentrations of each single monomer obtained with the two different dilution systems are very similar ($C_b/C_a \cong 1$, where C_a is the concentration obtained with water and C_b is the concentration with a 50/50 methanol/water solution), revealing a negligible effect of methanol in the recovery of residual monomers within the latex particles. The two gas chromatograms shown in Figure 2 are very similar, apart from the large methanol peak eluted at 4 min. For the type of matrix considered here, the use of an organic solvent, like methanol, to dilute the sample appears to be a disadvantage because of waste solvent recovery. Furthermore, the methanol peak interferes in the determination of substances having similar retention times, such as ethanol and acetaldehyde.

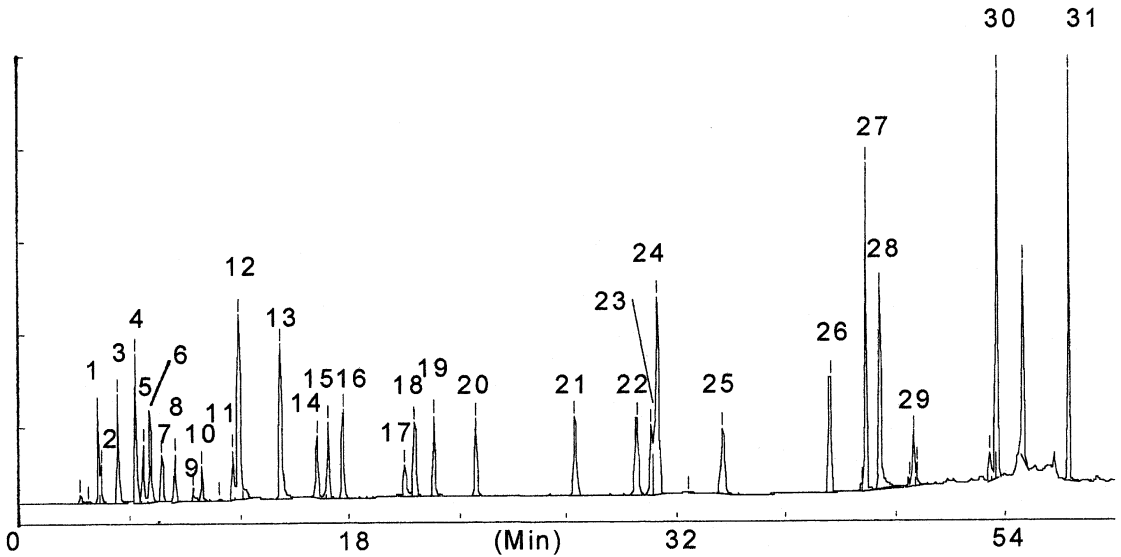

FIGURE 1 Example of the GC separation efficiency. Eluted peaks: (1) methanol, (2) acetaldehyde, (3) ethanol, (4) *i*-propanol, (5) acetone, (6) *t*-butanol, (7) methyl acetate, (8) acrylonitrile, (9) acetic acid, (10) vinyl acetate, (11) ethyl acetate, (12) *i*-butanol (internal standard), (13) *n*-butanol, (14) *t*-butyl acetate, (15) ethyl acrylate, (16) methyl methacrylate, (17) methacrylic acid, (18) toluene, (19) ethyl methacrylate, (20) *n*-butyl acetate, (21) ethyl benzene, (22) *n*-butyl acrylate, (23) *n*-butyl propionate, (24) styrene, (25) *i*-butyl methacrylate, (26) *n*-butyl methacrylate, (27) benzaldehyde, (28) 2-ethyl hexanol, (29) 2-hydroxy propyl methacrylate, (30) 2-ethyl hexyl acrylate, (31) butyldiglycol acetate.

TABLE II Comparison between the two different dilution systems

	$[C]_b/[C]_a$[a]	
Solutes	Mean ratio	Standard deviation
Acrylonitrile	1.1	0.1
Vinyl acetate	1.0	0.2
Ethyl acrylate	1.1	0.2
Methyl methacrylate	1.0	0.1
n-Butyl acrylate	1.1	0.2
Styrene	1.0	0.1

[a]a: water, b: 50/50 methanol/water.

Comparison Between the Two Methods

The results of the quantitative determinations achieved with the two methods expressed as the ratio between the concentration found with the FEHS and the liquid injection are summarized in Table III. A ratio value close to one means that the difference between the two types of analyses is quite small. Both methods allow the complete evaporation of the volatile phase, and only small quantities of substances are lost by condensation or absorption during the transfer to the injector.

A comparison between the data obtained from volatile free-latex matrices doped with different monomers (Table III, column A) and a series of samples selected from the standard and experimental products of Cray Valley Italia (Table III, column B) shows slightly greater FEHS recoveries for the former samples. In the first case the residual monomers are more superficially located, while in the second they are preferably absorbed into the core of the polymer particle. FEHS injection actually shows a slower evaporation rate because of the lower temperatures involved. Consequently, unreacted monomers are released with more difficulty, or probably they are lost because of polymerization or thermal degradation, decreasing the FEHS recovery factor. GC analysis carried out with the two techniques on the same sample are shown in Figure 3.

Vinyl acetate has the lowest [FEHS]/[LIQ] ratio, probably because of its partial thermal decomposition during the heating phase. This is confirmed by the higher amounts of acetaldehyde found in these determinations.

With respect to the other GC techniques, FEHS-GC has the disadvantage of being less useful for the determination of highly polar molecules, such as acetic, acrylic, and methacrylic acid, and acrylamide, which are generally underestimated when this technique is used. The

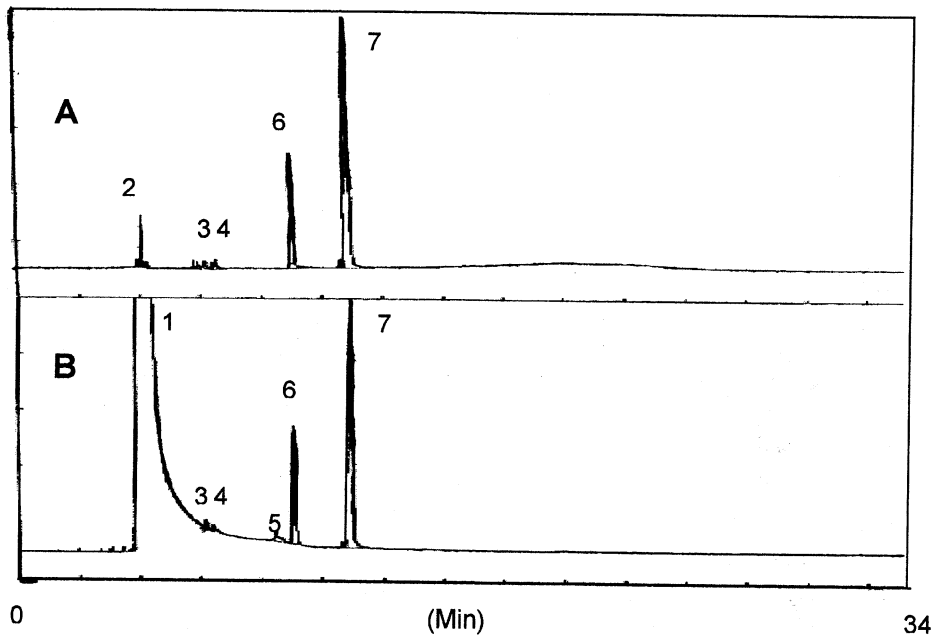

FIGURE 2 Gas chromatograms obtained by liquid injection of the same sample diluted with: (A) water, (B) 50/50 water/methanol solution. Eluted peaks: (1) methanol, (2) acetaldhyde, (3) acetone, (4) *t*-butanol, (5) acetic acid, (6) vinyl acetate, (7) *i*-butanol.

TABLE III Comparison between the two methods

Substances	A[a] conc. FEHS/ conc. LIQ.	A[a] σ^c	B[b] conc. FEHS/ conc. LIQ.	B[b] σ^c	No. of actual samples analyzed
Methanol	—	—	1.04	0.21	40
Acetaldehyde	—	—	1.00	0.27	37
Ethanol	—	—	1.10	0.21	29
i-Propanol	—	—	0.92	0.04	3
Acetone	—	—	0.90	0.19	35
t-Butanol	—	—	0.96	0.06	37
Acrylonitrile	0.89	0.05	0.81	0.10	14
Vinyl acetate	0.86	0.07	0.67	0.12	25
n-Butanol	—	—	1.12	0.26	42
Ethyl acrylate	0.86	0.08	0.79	0.10	17
Methyl methacrylate	1.01	0.07	0.79	0.15	5
n-Butyl acetate	—	—	0.91	0.21	28
n-Butyl acrylate	0.968	0.07	0.94	0.16	28
Styrene	0.951	0.11	1.00	0.14	15
n-Butyl propionate	—	—	0.95	0.19	23

[a]Results obtained from four latex samples, doped with 500 or 1000 ppm monomers.

[b]results obtained on actual samples.

[c]N-1 standard deviation of the [FEHS]/[LIQ] mean ratios.

phenomenom is mostly due to the high concentration of active centers localized in the vial and in the syringe. For injection volumes lower than 500 μL, a decrease is observed when the FEHS method is used. The reproducibility of the FEHS-GC method estimated from the standard deviations, inclusive of errors of both liquid injection and FEHS injection (Table III, column B), is comparable with that found in ASTM D 4827-93[7].

CONCLUSIONS

The full-evaporation head-space GC has been shown to be a useful analytical technique for the determination of free monomers and VOCs in water-based polymer dispersions. This method produces a gas phase having the same analytical composition as the sample, as happens with liquid injection. Its repeatability, on a wide range of monomer concentrations, is good and comparable to that shown by the test method

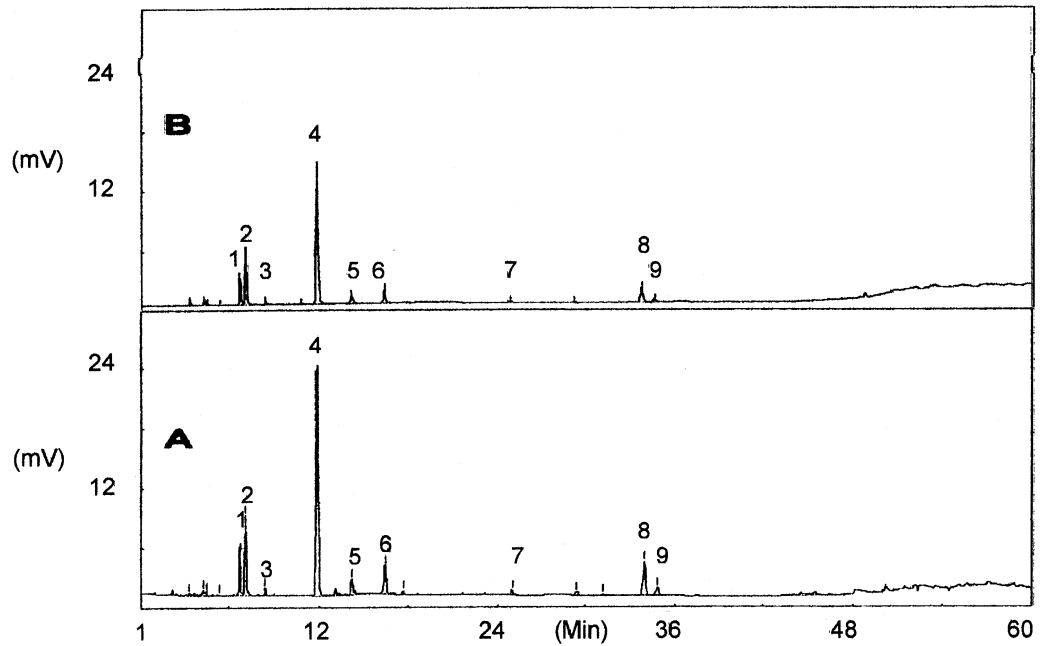

FIGURE 3 Gas chromatograms of the same sample obtained with the two different techniques: (A) liquid injection, (B) FEHS injection. Eluted peaks: (1) acetone, (2) *t*-butanol, (3) acrylonitrile, (4) *i*-butanol, (5) *n*-butanol, (6) unknown, (7) *n*-butyl acetate, (8) *n*-butyl acrylate, (9) *n*-butyl propionate.

reported in ASTM D 4827-93. The absence of syringe and injection line contamination makes the installation of an autosampler easier. The use of methanol or other organic diluents to improve the extraction of residual monomers from the latex particles is not necessary. FEHS GC is suitable for fully automated systems for on-line monitoring processes and quality control purposes. The few drawbacks of this technique are a slightly lower sensitivity than the liquid injection process and rather poor efficiency for the determination of highly polar molecules.

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