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Abstract

Two alternative RP-HPLC methods with fluorescence detection have been applied to quantify bisphenol A diglycidyl ether (BADGE; CAS No. 1675-54-3) in three different types of epoxy resins formulations, based on this monomer, used as a coating for food-contact packaging materials. Chloroform was chosen as a swelling solvent to extract BADGE from the finished product employing two different processes: one by refluxing for 4 hours, and the other at 50°C for two days. Both Isocratic and Gradient chromatographic methods were applied to determine this monomer at very low levels, the detection limit is 1.5 µg/L. The calibration lines had correlation coefficients no smaller than 0.998. Standard deviations obtained in the precision study were less than 9 %.

Key words: HPLC, bisphenol A diglycidyl ether, epoxy resins, food packaging.

Resumen

Se utilizaron dos métodos alternativos basados en RP-HPLC con detección de fluorescencia para cuantificar bisfenol A diglicidil éter (BADGE, No. CAS 1675-54-3) en tres tipos de formulaciones de resinas epoxi elaboradas con este monómero. Estas formulaciones se usan en la industria alimentaria, en alimentos enlatados, revistiendo la cara interna de la lata. Se utilizó cloroformo como solvente para extraer el BADGE del recubrimiento epoxídico de dos maneras: sometiendo el revestimiento a reflujo durante 4 horas o calentando el interior de la lata una vez rellena de cloroformo a 50° C durante dos días. Un método cromatográfico utiliza elución en gradiente y el otro usa régimen isocrático, ámbos permiten detectar BADGE hasta niveles muy bajos, el límite de detección es de 1.5 µg/L. Los coeficientes de correlación de las rectas de calibrado son superiores a 0.998 y las desviaciones estándar de las precisiones de los dos métodos están por debajo de 9 %.

Palabras clave: HPLC, bisphenol A diglycidyl ether, resinas epoxi, envases alimentarios.

Resumo

Aplicáronse dous métodos alternativos baseados en RP-HPLC con detección de fluorescencia para cuantificar bisfenol A diglicidil éter (BADGE, No. CAS 1675-54-3) en tres tipos de formulacións de resinas epoxi elaboradas con este monómero. Estas formulacións empréganse na industria alimentaria nos alimentos enlatados, revestindo a cara interna da lata. Utilizouse cloroformo como solvente para extraer-lo BADGE do recubrimento epoxídico de dúas maneiras: sometendo ó revestimento a reflujo durante 4 horas ou calentando o interior da lata unha vez rechea de cloroformo a 50° C durante dous días. Un método cromatográfico emprega elución en gradiente e o outro usa réxime isocrático, ámbolos dous permiten detectar BADGE ata niveis moi baixos, o límite de detección é de 1.5 µg/L. Os coeficientes de correlación das rectas de calibrado son superiores a 0.998 e as desviacións estándar das precisións dos dous métodos están por debaixo do 9 %.

Palabras chave: HPLC, bisphenol A diglycidyl ether, resinas epoxi, envases alimentarios.

INTRODUCTION

Bisphenol A diglycidyl ether (BADGE), oxirane, 2,2' - [(1-methyl ethylene)bis-(4,1-phenyleneoxymethylene)]bis-, CAS Component Name (CAS Registry Number: 1675-54-3), is the reaction product of the bisphenol A with the epichlorohydrin. It is used as starting material in epoxy resins employed in the production of laminates structures for food contact. These epoxy resins are used mainly in paints and lacquers for coating foodstuff containers ranging from small cans for food to large metal or concrete vats or tanks for water, fruit juices, wine, oil or other liquids.

The problem of the determination of the BADGE in aqueous and fatty simulants has been treated thoroughly by us in previous papers (Paseiro Losada *et al.*, 1991a; 1991b; 1992; 1993; 1997; 1999 and Simal Gándara *et al.*, 1993).

The quantitative analytical determination of residual BADGE in plastic materials involves as its first step, prior to measurement, the total extraction of BADGE from the finished product. Our own experience that a swelling solvent be used led us to choose extraction into chloroform products (Paseiro Losada *et al.*, 1991a), in which BADGE is very soluble and the polymer reference material used in method development is insoluble. The chosen extraction technique was boiling under reflux.

For the subsequent measurement step, we considered it appropriate to exploit as far as possible the experience gained in the development of methods for analysing BADGE. Thus, all the considerations concerning the determination of BADGE by HPLC with fluorescence detection, the choice of excitation and emission wavelengths and other working conditions for chromatography that were expressed in a previous paper (Paseiro Losada *et al.*, 1997), are relevant to the present. Some authors (Lambert and Larroque, 1997) use the same HPLC method proposed by us (Paseiro Losada *et al.*, 1997) and other authors apply different chromatographic techniques (Bronz *et al.*, 1998; Biedermann and Grob, 1998; Biedermann *et al.*, 1996 and Philo *et al.*, 1997) to analyse BADGE.

In view of the performance of the measurement technique (which allows identification and quantification of BADGE at the $20 \mu\text{g} \times \text{L}^{-1}$ level), we decided to extract with 50 mL of chloroform per grame of polymer material, apart from the other extraction technique, boiling under reflux.

Special Difficulties with Thermostable Plastic Coatings

The main analytical difficulty posed by thermostable plastic coatings is the obtaining representative samples of sufficient weight, since the coatings exist as films ranging from a few to several hundred microns in thickness and adhere strongly to their support. In practice,

it is impossible to obtain by mechanical means (scraping, abrasion, etc.) samples which include material from the deeper layers of the coating but that do not include support material especially in the case of films lining small food cans. We, therefore, suggest three approaches to evaluation of the BADGE content of such coatings, one based on mechanical sampling and two alternatives.

When the nature of the film allows, mechanical means, (i.e., by using a metal rasp or some other suitable tool) should be used to obtain a sample of adequate weight.

Coating materials that can be painted on and adhered adequately to a plate made of glass or some other inert material (e.g. polymer coatings for large tanks) can be appropriately installed on a previously weighed plate (e.g. by painting and curing following the manufacturer's instructions), the coated plate re-weighed, the sample weight calculated by difference.

For coatings that for technical reasons must be tested *in situ* on their intended support (e.g., food cans), the root problem is that the weight of the coating is unknown.

We suggest that in these cases chloroform be employed as a "special" food simulant and that the concentration of monomer in this special simulant be determined under suitably standardized conditions of contact time and temperature ensuring the extraction and stability of all unpolymerized monomer.

MATERIALS AND METHODS

Chemicals, Solvents and Solutions

The BADGE used was an epoxy resin named Epikote 828 (from Shell; Zaragoza, Spain), purified (>99%) by Gairesa as described (Paz-Abuín *et al.*, 1990).

Stock and dilute stock solutions of BADGE were prepared as previously described (Paseiro Losada *et al.*, 1999):

A stock solution of BADGE standard was prepared in tetrahydrofuran at a concentration of 1.0 mg/mL. 100 mg of BADGE was accurately weighed into a 100 mL volumetric flask, then diluted to the mark with tetrahydrofuran.

Dilute stock solutions of BADGE standard at a concentration of 1.0 $\mu\text{g}/\text{mL}$. Transfer 10 mL of the stock solution of BADGE standard into a 100-mL volumetric flask and dilute to volume with 90%(v/v) methanol. Transfer 10 mL of this solution into a 100-mL volumetric flask and dilute to volume with 90%(v/v) methanol; transfer 10 mL of the resulting solution into a 100-mL volumetric flask and dilute to volume with 90%(v/v) methanol. The final 1.0 μg per mL BADGE solution was transferred to a

250-mL cylindrical flask and store at -20 °C. The solution should not be allowed to remain at room temperature for more than a few minutes.

Preparation of calibration solutions: 0.5, 1, 2, 3 and 4 mL of the dilute stock solution of BADGE standard at a concentration of 1 µg/mL was transferred to a series of 100-mL volumetric flasks and fill to the marks with 90% (v/v) aqueous methanol to obtain 5, 10, 20, 30 and 40 µg per litre BADGE solutions. As these solutions are not stable at room temperature they should be used immediately. Blanks were prepared by transferring 0.02 mL of THF to a 100-mL volumetric flask and fill to the mark with 90% (v/v) aqueous methanol.

50 µL of each calibration sample was injected into the chromatograph (triplicate). The area of the BADGE peak was determined in the resulting chromatograms.

Demineralized water was obtained from a Milli-Q system (Millipore Corporation). Chloroform (Ref. 10077) from BDH (Poole, Dorset England), acetonitrile HPLC supragradient grade (Ref. Ac 331) and 90% (v/v) Methanol analytical quality from Scharlau (Barcelona, Spain).

Microfilters MFS-13, PTFE membrane, diameter 13 mm, pore size 0.5 µm, from MFS (California, USA).

Apparatus and Chromatographic Conditions

They have been used the same as in other issues (Paseiro Losada *et al.*, 1997, 1999):

A liquid chromatograph system from Spectra-Physics, consisting of binary pump with helium degassing kit with fluorescence detector (excitation wavelength 225 nm and emission wavelength 305 nm) was used. Column: length 15 cm, internal diameter 4.6 mm, packed with 5 µm Spherisorb ODS 2.

An ultraviolet detector (wavelength 225 nm) with scanning function on eluting peaks, was used only for confirmation, i.e. chromatograms are obtained by both fluorescence and UV detection (UV detector was located in series and in front of the fluorescence detector), and the identity of BADGE is confirmed by the ratio between the areas of its peaks in the two chromatograms (Paseiro Losada *et al.*, 1997).

Elution program for Gradient Method: gradient elution consisted of a 2-min Isocratic elution with acetonitrile-water (30:70) (v/v), a 18-min linear gradient to 80% acetonitrile, a 3-min linear gradient to 100% acetonitrile and 2-min isocratic elution at 100% acetonitrile. Flow rate: 1 mL/min. Typical retention time for BADGE is 17.4 min. Elution program for Isocratic Method: isocratic elution with acetonitrile-water (65:35) (v/v). Flow rate: 1 mL/min. Typical retention time for BADGE is 5.3 min.

Furthermore a reflux apparatus was necessary: 250 mL of flat-bottomed flask, 29/32. Water-cooled Liebig condenser, effective length 400 mm, cone 29/32. Hot plate with sand bath.

Method performance with test samples

Polymer

The polymer coating tested was an epoxy paint based on a BADGE epoxy resin with *m*-xylylenediamine as a curing agent. Its intended use is as a coating on food-storage vessels.

Quantity Maximum test

Glass discs, each of total surface area 1.22 dm², were weighed (W_b), painted with the polymer coating on one side, left curing for 24 h at room temperature, painted on the other side, cured at room temperature for 5 days and then re-weighed (W_a). The weight of coating (M) was calculated as the difference, $W_a - W_b$. The samples so prepared were subjected to procedures described in the Introduction under *Special difficulties with thermostable plastic coatings*, in two ways:

A clean metallic file was used to scrape off a coating sample weighing approximately 300 mg of ground sample into a dry flat-bottomed flask, add 15 mL of chloroform by pipette, and weigh again to the nearest 0.01 g. Reflux for 4 hours on a plate and cool to room temperature. Filter a few milliliters of the solution, and pipette 1 mL of the solution into a vial. Remove the solvent in the vial under a stream of nitrogen and dissolve the residue in 1 mL of 90% (v/v) methanol in an ultrasonic bath, and pass the resulting solution through a microfilter.

The glass discs were placed in a sheet of saturated paper. Wrap the glass plate in the paper and strike it with a small mallet to break it into a pieces with maximum diameter of less than 2 cm. Transfer all the glass to the flat-bottomed flask, add 150 mL of chloroform, and proceed as above.

Migration from other polymer formulations (food cans)

As well as testing the above-mentioned BADGE-based polymer paint as described, we also tested three other epoxy formulations for use as coatings on food cans:

- Formulation Type 1: special coating for cans intended to contain sulfurous products; epoxy - phenolic; drying, 15 min at 205°C; surface density of dry film, 4-6 g m².
- Formulation Type 2: epoxy-phenolic; drying, 15 min at 205°C; surface density of dry film, 4-6 g m².
- Formulation Type 3: epoxy; drying, 15 min at 195°C; surface density of dry film, 14-18 g m².

All these formulations must be treated as coatings that for technical reasons must be tested *in situ*. They were tested in two-piece or three-piece cans with an interior surface/volume ratio of approx. 1 dm² × 100 mL⁻¹. The cans were filled with chloroform and the lids were mechanically sealed.

Kinetics of BADGE extraction conditions

With chloroform at 50°C: A glass disc with an epoxy-amine coating weighing approximately 3 g was immersed in 150 mL of chloroform in a hermetic glass cell maintained at 50 °C (close to, but below, the boiling point of chloroform, the intention being to reduce extraction time to a minimum).

In refluxing chloroform: 0.5 mL samples were withdrawn after 0, 1, 2, 4, 8, 12, 24 and 48 hours at 50°C (or 0.5, 1, 2, 4, 8 and 12 hours at refluxing) and were diluted with 90% (v/v) methanol and analysed by HPLC.

RESULTS AND DISCUSSION

Calibration line

The calibration lines for both Isocratic and Gradient methods had correlation coefficients no smaller than 0.998. To verify the effective detection limit calculated from the calibration lines, a 1.5 µg/L BADGE solution was run in triplicate. The signal-to-noise ratio of the BADGE peak was about 6. Noise was measured as the maximum amplitude of the chromatogram of a blank between 4.8 and 5.8 minutes (Isocratic Method) or 16.9 and 17.9 minutes (Gradient Method).

Precision

In view of the unavailability of a reference polymer material containing BADGE at a established quantity, six solutions of BADGE were prepared in chloroform at a concentration of approximately 20 (µg BADGE) × (L⁻¹ chloroform), which for a sample: extraction ratio of 1 g: 50 mL is equivalent to 1 mg × kg⁻¹; the sample solutions were prepared as above, except that chloroform was used instead of 90% methanol in making up both dilute BADGE stock solution and the six final samples. The six samples and the corresponding blanks were processed passing a few milliliters of the solution through a filter and 1 mL of the filtered solution into a vial; the solvent in the vial was removed under a stream of nitrogen, and the residue dissolved in 1 mL of 90% (v/v) methanol, and were run in duplicate. Mean recovery was 92.3% for the Isocratic Method and 98.4% for the Gradient Method, with standard deviations of 4.1% and 8.2% respectively.

Confirmation

The confirmation of the identity of BADGE was carried out as has been reported in previous issues (Paseiro Losada *et al.*, 1997; 1999).

Method performance with test samples

Migration from polymer (epoxy amine formulation).

Triplicate polymer samples were separately treated in accordance with both ways, explained in experimental section, and the BADGE content of each was then determined in duplicate after adequate dilution of the final methanolic solution with 90% (v/v) methanol

so as to avoid saturation of the fluorescence detector; blanks obtained from chloroform samples refluxed for 4 hours were also run.

The mean measured BADGE content of the polymer was 332 mg × kg⁻¹, or 1.24 mg × dm², and 373 mg × kg⁻¹, or 1.40 mg × dm², by both isocratic and gradient methods, with standard deviations of respectively 10.2% and 4.3%. The total average amount of migrants (BADGE + other migrants) was 3376 mg × kg⁻¹ or 11.5 mg × dm². Typical chromatograms obtained for the sample without dilution are shown in Figure 1.

The Gradient Method chromatogram shows both the BADGE peak and other peaks, most of which probably correspond to BADGE derivatives (see below). Most peaks have retention times longer than 15 min, whereas most substances in the migrant-containing aqueous food simulants obtained in migration experiments have retention times shorter than 15 min. This suggests that the peaks in the migration solution chromatograms are due to substances that have less affinity for the stationary phase than the substances responsible for corresponding peaks in the extract chromatograms, and hence that the former substances are probably more polar derivatives of the latter. For example, BADGE derivatives and other epoxy compounds appearing in the extract chromatograms could be hydrolyzed to more polar substances upon migration into aqueous food simulants.

Migration from other polymer formulations (food cans)

Migration testing was then performed for 10 days at 40 °C and for 2 days at 50 °C (the latter conditions were employed in the light of prior kinetic results summarized below; see Kinetics of BADGE extraction with chloroform at 50 °C). Typical chromatograms diluted ten-fold obtained after 2 days at 50 °C are shown in Figure 1 (those obtained after 10 days at 40 °C are essentially similar). The hypothesis that many of the unidentified peaks correspond to epoxy compounds is supported by the same arguments as were developed above in BADGE epoxy paint, and the fact that, on the whole, retention times are longer in these chromatograms than in the corresponding chromatograms of aqueous migration solutions obtained in 30 min migration experiments carried out at 121 °C (Paseiro Losada *et al.*, 1999). Chromatogram shown in Figure 1 correspond to solutions 300 times more dilute than is necessary for determination of 20 µg × L⁻¹ of BADGE (equivalent to 1 mg × kg⁻¹ in polymer). The migration results for the three different types of epoxy formulations are listed in Table 1.

Kinetics of BADGE extraction

The extraction curves are shown in Figure 2. BADGE concentration remained constant after 12 hours at 50°C (or 2 hours at refluxing), showing maximum extraction of BADGE. In view of the nature of the sample and solvent, it may be assumed that all non-polymerized BADGE was extracted. For the proposed method we nevertheless prescribe an extraction time of 48 hours at

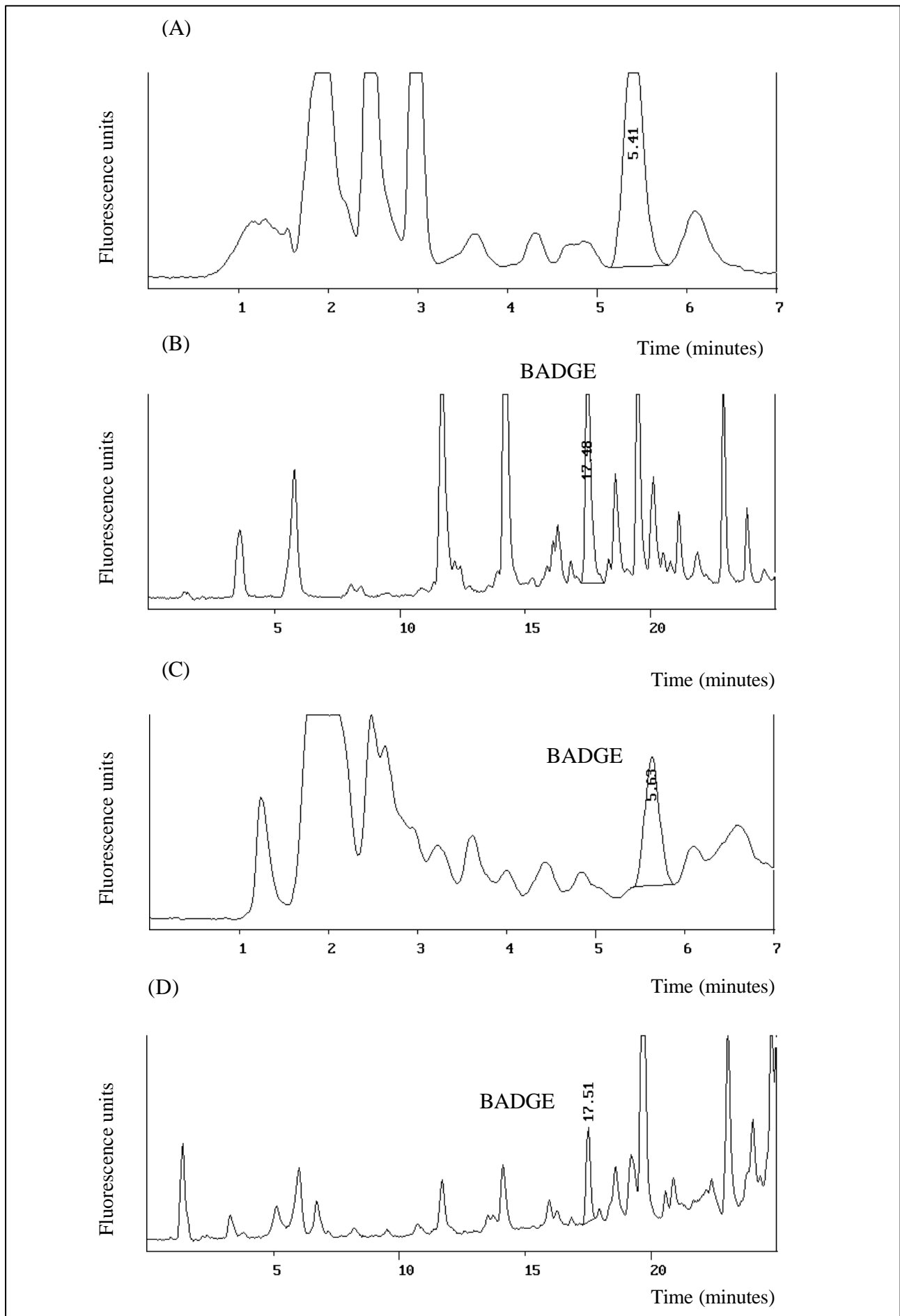


Figure 1. Chromatograms with monomer extracted from the test material by 4 hours reflux applying: (A) Isocratic method and (B) Gradient method and chromatograms of epoxy can coating Type 3 after migration test 2 days at 50°C processed by (C) Isocratic method and (D) Gradient method.

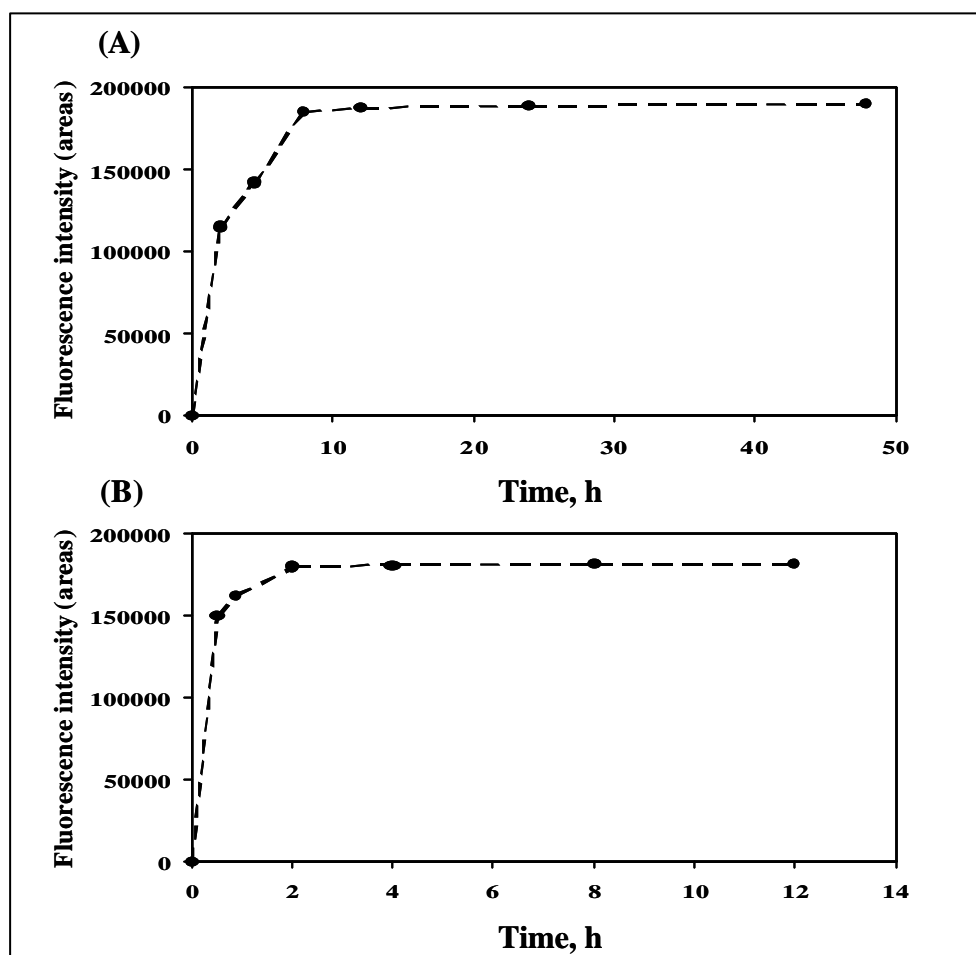


Figure 2. Kinetics of BADGE extraction with chloroform applying Gradient Method: (A) at 50°C and (B) refluxing.

Table 1.-Migration results corresponding to quantity maximum for the epoxy formulations tested after 2 days at 50°C, expressed as $\mu\text{g} \times \text{L}^{-1}$ of simulant, $\text{mg} \times \text{dm}^{-2}$ of plastic material and $\text{mg} \times \text{kg}^{-1}$ of epoxy formulation. *The concentrations of "Other migrants" are expressed in BADGE.

Simulant	Analyte	2 days at 50°C Conc measured ($\mu\text{g} \times \text{L}^{-1}$)			2 days at 50°C Conc measured ($\text{mg} \times \text{dm}^{-2}$)			2 days at 50°C Conc measured ($\text{mg} \times \text{kg}^{-1}$ resin)		
		Type 1	Coating Type 2	Type 3	Type 1	Coating Type 2	Type 3	Type 1	Coating Type 2	Type 3
Chloroform	BADGE + Other migrants*	267 5466	694 14893	313 6621	0.027 0.547	0.069 1.489	0.031 0.662	540 10940	1380 29780	620 13240

50°C (or 4 hours at refluxing) as striking a plausible balance between laboratory convenience and the provision of a reasonable guarantee of the total extraction of BADGE from all kinds of BADGE polymer, not just the particular material used in developing the method.

Stability of BADGE in refluxing chloroform

The stability of BADGE during the extraction process was investigated by carrying out repeatability experiments in which chloroform was spiked with BADGE at concentrations of 10, 20 and 40 $\mu\text{g} \times \text{L}^{-1}$ and refluxed for 4 hours before determination of BADGE. Mean recovery was 87.1% for the Isocratic Method and 93.7% for the Gradient Method, and the respective standard deviations were 8.2% and 9.2%

CONCLUSIONS

1. We developed a method for the extraction of BADGE from polymer materials that allows determination of BADGE in polymer at very low levels by means of either the Gradient or Isocratic HPLC methods described in preceding articles (Paseiro Losada *et al.*, 1997; 1999). The advantages and disadvantages of each methods were discussed.
2. For the special case of coatings which for technical reasons must be tested on their intended support, thereby making it impossible to determine the weight of material being tested (which in turn makes it impossible to express the extracted quantity of BADGE as a concentration), we propose that

migration tests be performed using chloroform as a "special" food simulant under conditions preventing significant degradation of BADGE.

- The epoxy formulations studied in this work which are intended as coatings for large tanks or small metallic cans contained considerable quantities of chloroform-extractable epoxy compounds, most of which appeared to be related to BADGE (presumably being oligomers or the products of side reactions occurring during reaction between bisphenol A and epichlorohydrin). To an extent depending on temperature and contact time, these compounds also migrate into aqueous food simulants, where most are converted to more polar compounds, probably as the result of their epoxy rings being opened by hydrolysis reactions analogous to those already known to affect BADGE itself.

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