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GAS CHROMATOGRAPHIC DETERMINATION OF VINYLIDENE CHLORIDE MONOMER IN PACKAGING FILMS AND IN FOODS

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SUMMARY

Headspace electron-capture–gas chromatographic methods are described for the quantification of vinylidene chloride monomer in poly(vinylidene chloride) containing films and in film-packaged foodstuffs. Quantification of vinylidene chloride was possible at levels down to 0.001 mg/m^2 in the films and 0.005 ppm in the foodstuffs. The results of a small survey of the amounts of this compound in packaging films and foodstuffs purchased from retail outlets are reported.

INTRODUCTION

The detection of vinyl chloride monomer in foodstuffs packaged in poly(vinyl chloride) (PVC)[1] coupled with concern over toxicity has led to a proliferation of surveys of levels of vinyl chloride in PVC[2–5] and in foods[6–10] and has consequently initiated interest in the possible presence of other monomer residues in food packaging materials. Residual acrylonitrile levels have been measured in acrylonitrile–butadiene–styrene resins, foods and simulants[11–14]; styrene and other aromatic volatiles have been estimated in polystyrene[15,16], and attempts have been made to estimate levels in foods[17,18]. Similarly, attention has also been directed towards residual vinylidene chloride (VDC) monomer levels in poly(vinylidene chloride) (PVDC) films[19,20] and in food simulants[21–23], but published methods for estimating residual VDC[19,20,23] have not been universally applicable to all PVDC film materials and there have been no reports of current levels of monomer in food grade packaging materials or of the detection of VDC in film-packaged foodstuffs.

PVDC is widely used as a coating on cellulose or polypropylene for the packaging of snack products such as potato crisps, for biscuits, cakes etc. and as a copolymer with PVC in the packaging of patés, cooked sausages and processed cheeses in the form of "chub" packs. Existing methodology for the estimation of residual VDC in PVDC has involved either total dissolution of the film in an appropriate solvent[19,23] or alternatively dissolution of the film coating[20] and quantification by gas chromatography (GC) using a flame-ionization detector (FID)[20], or an electron-capture detector (ECD) with confirmation by single-ion mass spectrometry[19]. However both these

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procedures have disadvantages in that total dissolution is limited to PVC–PVDC copolymers and with solvent treatment of PVDC on insoluble substrates it is difficult to ensure complete extraction and the procedure is time-consuming. A more widely applicable technique for films is that of the "hot-jar" method[24] (*i.e.* heating the film in a sealed container and sampling the headspace gas) which has been used previously for the estimation of solvent residues in films[25,26]. The present work shows that by application of this principle it is possible to estimate the levels of residual VDC in films down to a limit of 0.001 mg/m^2 by electron-capture gas–solid chromatography. Identification of VDC has been confirmed by single-ion mass spectrometry.

For estimation of VDC in foodstuffs a headspace electron-capture chromatographic procedure similar to that reported for trichloroethane[27] was employed enabling quantification down to a limit of 0.005 ppm. Using these techniques data are reported on current levels of VDC in films and foodstuffs purchased from retail outlets.

EXPERIMENTAL

Materials

VDC was purchased from Koch-Light Labs. (Colnbrook, Great Britain) and was re-distilled prior to use. Samples of unconverted films were provided by ICI Plastics (Welwyn Garden City, Great Britain) and items of foodstuffs (packaged in contact with PVDC-containing film) purchased locally from retail outlets. For other investigations a number of identical bags containing biscuits were prepared in the laboratory by heat sealing PVDC-coated polypropylene film. Storage for up to 60 days was at ambient temperature on an open shelf. Aadditionally some bags (containing porato crisps) manufactured from unprinted PVDC-coated polypropylene (containing an unusually high level of VDC) were supplied by Smiths Food Group (London, Great Britain). Storage was for approximately 25 days prior to analysis.

Identification of films

Packaging films from retail packs were identified from infrared spectra obtained by transmission and multiple total internal reflectance, by comparing with reference film materials and with published infrared spectra[28].

Determination of VDC in packaging films

Sample preparation. The packaging films from retail packs were sampled immediately after purchase. After removal of the contents the inner surfaces of the films were wiped with soft tissue to remove grease and visible food residues and 250-cm^2 sections of film were cut into narrow strips, crumpled into 160-ml hypovials and sealed with rubber septa. For unconverted packaging films, samples were taken from inner layers of the roll immediately upon receipt of the film. All samples were stored at −15°C prior to analysis.

Gas chromatography. A Pye Series 104 chromatograph equipped with a ^{63}Ni ECD was used in a pulsed mode with a spacing of 150 μS under the following conditions: glass column (2.7 m × 0.2 cm I.D.) packed with 80–100 mesh Porasil D; carrier gas (oxygen-free nitrogen) flow-rate, 20 ml/min with a make-up gas to the ECD of

60 ml/min; detector oven temperature, 200°C; injector temperature, 150°C. Column temperature, isothermal at 80°C until elution of the VDC peak (approximately 5 min) then heated rapidly to 250°C for 30 min to remove further high-boiling components.

Film analysis. Film samples contained in glass hypovials were heated at 120°C in an air-circulating fan oven for 30 min prior to analysis. Headspace vapour injections (1 ml) were removed manually using a 2 ml Pressure-Lok gas-tight syringe (Precision Sampling, Baton Rouge, LA, U.S.A.) and were injected onto the gas chromatograph under the conditions described above. For calibration standards a solution of VDC in ethyl acetate (0.1 μg/μl) was prepared, microlitre amounts being injected into empty hypovials. Estimation of VDC in the film samples was based on peak height measurement and direct proportion to a calibration standard chromatographed immediately prior to the sample.

Confirmation of identity of VDC in film was carried out by single-ion monitoring mass spectrometry. A DuPont Model 21-490B mass spectrometer interfaced with an all-glass jet separator to a Varian 2700 gas chromatograph was employed and was tuned on the molecular ion of authentic VDC (*m/e* 96). GC conditions were as previously except that a 3 m × 0.2 cm I.D. stainless steel column packed with 80–100 mesh Porasil D was employed. A positive signal for *m/e* 96 of correct retention time for VDC was taken as confirmation of identity.

Determination of VDC in food products

Sample preparation. Snack products (*e.g.* potato crisps) were crushed in the bags, and biscuits were broken to small pieces and samples of 5.0 ± 0.05 g were rapidly weighed into 24-ml hypovials and sealed with butyl rubber septa. For cooked meat and cheese products purchased in chub packs samples were taken both from the outer surfaces in contact with the plastic by cutting a thin section with a scalpel, or the total contents of a chub pack were ground under liquid nitrogen to a fine powder ensuring thorough mixing; in both cases 5.0-g samples being weighed into hypovials. All samples were held at −15°C prior to analysis.

Gas chromatography. Identical apparatus and conditions to those described previously.

Food analysis. Food samples contained in glass hypovials were heated at 60 ± 1°C in a waterbath for a minimum of 90 min, prior to analysis. As previously, 1 ml headspace vapour injections were removed manually, and the GC column was "baked-out" where necessary between sample injections.

A standard VDC in air calibration mixture of known concentration (*ca.* 1.0 μg/ml) was prepared by injection of a known weight of VDC into an all-glass 1-litre storage bottle (Aldrich, Milwaukee, WI, U.S.A.) fitted with PTFE tap and silicone rubber septa. After leaving for 15 min to ensure uniform distribution of the VDC, vapour samples were removed with a gas-tight syringe and injected into the hypovials containing the foodstuff. Before analysis in order to allow equilibrium partition to establish between VDC and the foods it was found to be important for spiked samples to stand overnight at room temperature.

Estimations of VDC in foods were based on peak height measurements by either direct proportion to a spiked sample of an identical foodstuff which had not been previously in contact with plastic packaging or by the method of standard additions to the film-packaged food samples.

RESULTS AND DISCUSSION

The headspace technique described for the determination of VDC in a variety of packaging films was adequate for quantification down to 0.001 mg/m^2; this is equivalent to between 0.04 and 0.06 ppm depending on the grammage of the film. In order to employ a single chromatographic column for all types of films it was found essential to use electron-capture as the method of detection. Non-electron capturing interference peaks from films obtained from retail packaging gave erroneously high answers for VDC levels when an FID was used with a Porasil D column. Although a change of column to Carbopack C could lead to resolution of interfering components on the FID this was not successful for all types of films examined from retail food packaging. As well as specificity the ECD also allowed greater sensitivity compared with the FID.

In order to ascertain that heating PVC–PVDC copolymer film for 30 min at 120°C was adequate for complete vaporisation of VDC into the headspace, esti-

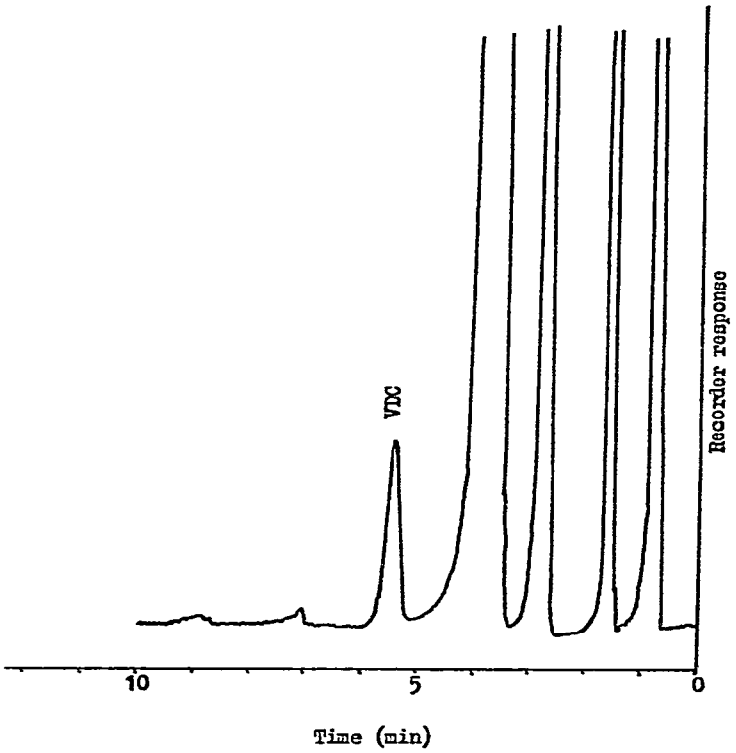

Fig. 1. Headspace chromatogram from above heated PVDC-coated polypropylene potato crisp bag. Column 2.7 m × 0.2 cm I.D. packed with 80–100 mesh Porasil D, flow-rate 20 ml/min, temperature isothermal at 80°C. ECD operated in pulsed mode at 150 μsec with make-up gas of 60 ml/min; (attenuation 2·10^2).

mations of VDC levels made by the "hot jar" technique were compared with those obtained by total dissolution in dimethylacetamide, equilibration and then headspace sampling. Levels of VDC by total dissolution were found to be comparable to those obtained by direct heating of the films. The copolymer represents the extreme situation for vapourisation of VDC; it is the thickest of the films examined and additionally the VDC is dispersed throughout the film. By contrast the VDC in coated films would be expected largely in the surface layer, although there must inevitably be some diffusion into the substrate. A typical chromatogram is shown in Fig. 1 for a PVDC-coated polypropylene potato crisp bag after direct heating of the film and headspace sampling.

Table I shows the results of a small survey of levels of VDC in both packaging films and foodstuffs purchased from retail outlets during October 1978. Levels of VDC in PVDC-coated cellulose film were all below the limit of detection (*i.e.* < 0.001 mg/m^2), and for the PVDC-coated polypropylene and PVC–PVDC copolymer levels ranged from < 0.001 to 0.022 mg/m^2. As unconverted film of PVDC-coated polypropylene from the manufacturer at this time contained levels of 0.02–0.04 mg/m^2 it was of some interest to examine the loss of VDC during bag manufacture and exposure to atmosphere during prolonged storage. Samples of film were taken by ex-

TABLE I

OBSERVED LEVELS OF VDC MONOMER IN A VARIETY OF RETAIL PACKAGING FILMS AND FOOD PRODUCTS

PVDC/PP, PVDC-coated polypropylene film; PVDC/cel, PVDC-coated cellulose film; PVDC–PVC, homogeneous PVDC–polyvinylchloride copolymer film.

Product	*Film type*	*Level VDC in film*		*VDC level in food (ppm)*
		mg/m²	*ppm*	
Biscuits:				
Ginger cookies	PVDC/PP	0.018	1.02	<0.005
Currant	PVDC/PP	0.010	0.54	<0.005
Bourbon	PVDC/PP	0.004	0.24	<0.005
Nut cookies	PVDC/cel	<0.001	<0.04	<0.005
Almond	PVDC/cel	<0.001	<0.04	<0.005
Shortcake	PVDC/cel	<0.001	<0.04	<0.005
Custard cream	PVDC/PP	<0.001	<0.06	<0.005
Cakes:				
Swiss roll	PVDC/cel	<0.001	<0.04	<0.005
Snack products:				
Potato crisps	PVDC/PP	0.002	0.14	<0.005
Flavour extruded potato	PVDC/PP	0.022	1.26	<0.005
Flavour extruded potato	PVDC/PP	0.003	0.20	<0.005
Cooked meats:				
Black pudding	PVDC–PVC	0.008	0.18	0.005–0.01
Liver pate	PVDC–PVC	0.013	0.28	0.005–0.01
Polony	PVDC–PVC	0.002	0.04	<0.005
Bacon and liver pate	PVDC–PVC	<0.001	<0.02	–
Cheeses:				
Smoked	PVDC–PVC	<0.001	<0.02	<0.005

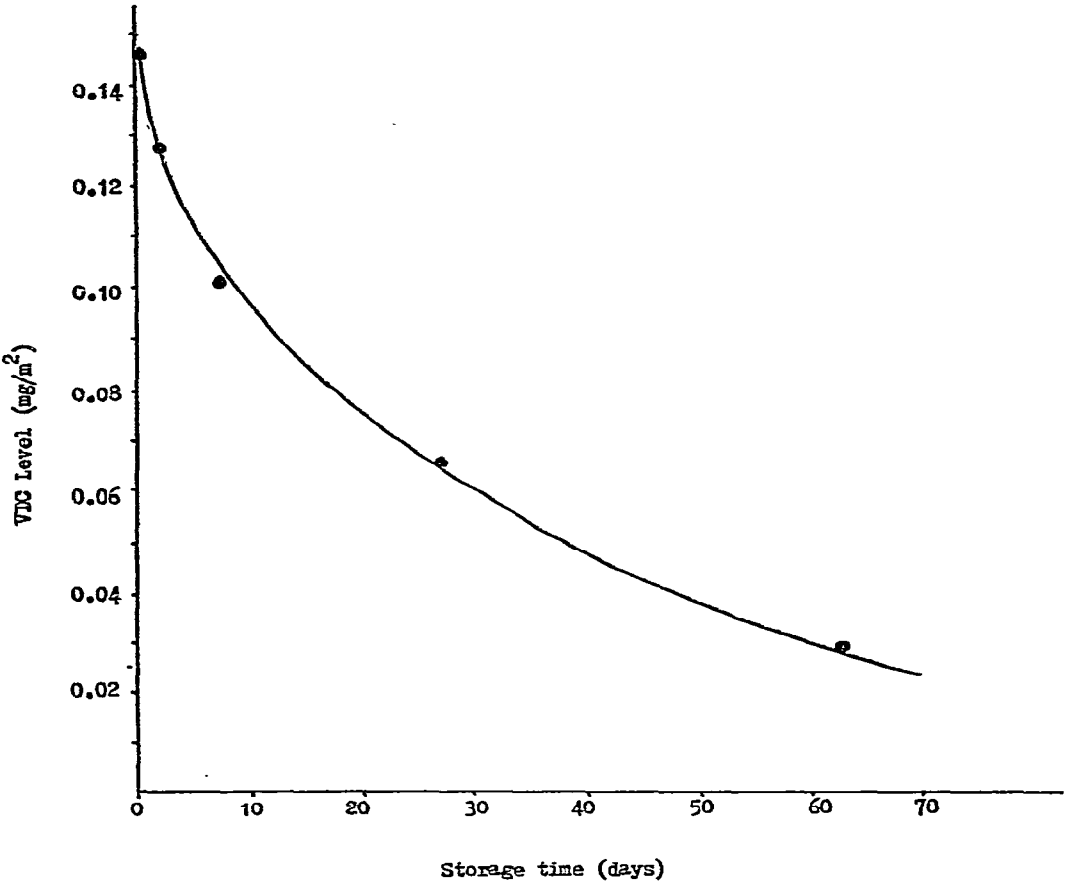

Fig. 2. Changes in residual VDC levels in PVDC-coated polypropylene biscuit packs on storage at ambient temperature.

TABLE II

LEVELS OF VDC MONOMER IN SPECIALLY MANUFACTURED* FILM BAGS AND POTATO CRISP CONTENTS AFTER 30 DAYS STORAGE

Product sample number	*VDC level in unconverted film*		*VDC level in bag*		*VDC level in potato crisps (ppm)*	
	mg/m²	*ppm*	*mg/m²*	*ppm*	*Calibration curve*	*Standard addition*
1	0.022	1.24	0.003	0.16	0.015	0.01–0.02
2	0.022	1.24	0.003	0.16	0.010	0.005–0.01
3	0.022	1.24	0.003	0.16	0.025	0.02–0.03
4	0.022	1.24	0.002	0.12	0.025	0.02–0.03

* These bags and potato crisps were not retail packs.

amining laboratory manufactured bags containing biscuits, at intervals over a total of 60 days and the levels of VDC were estimated. The decrease in VDC levels is shown in Fig. 2, from an unusually high initial level (0.146 mg/m^2) nearly 80% was lost during this period.

For estimations of VDC in foods the electron-capture headspace technique was adequate for quantification to a limit of 0.005 ppm. No problems of interference were experienced for the variety of food types shown in Table I. Typical chromatograms are shown in Fig. 3 for potato crisps which had never been in contact with plastic packaging and which contained no detectable VDC and for potato crisps containing a measurable quantity of monomer (see Table II). In order to achieve this degree of sensitivity it was essential to exclude from the vials the laboratory atmosphere which might have contained interfering components and therefore foodstuffs were sampled and vials sealed in an area remote from the laboratory. Biscuits, cakes, snack products and cheeses did not contain detectable amounts of VDC (< 0.005 ppm), but for some of the cooked meat products monomer was present in the range 0.005–0.01 ppm the highest levels being found in the edge samples.

Table II shows results from a small exercise in which specially manufactured PVDC-coated polypropylene bags filled with potato crisps were stored for 30 days at

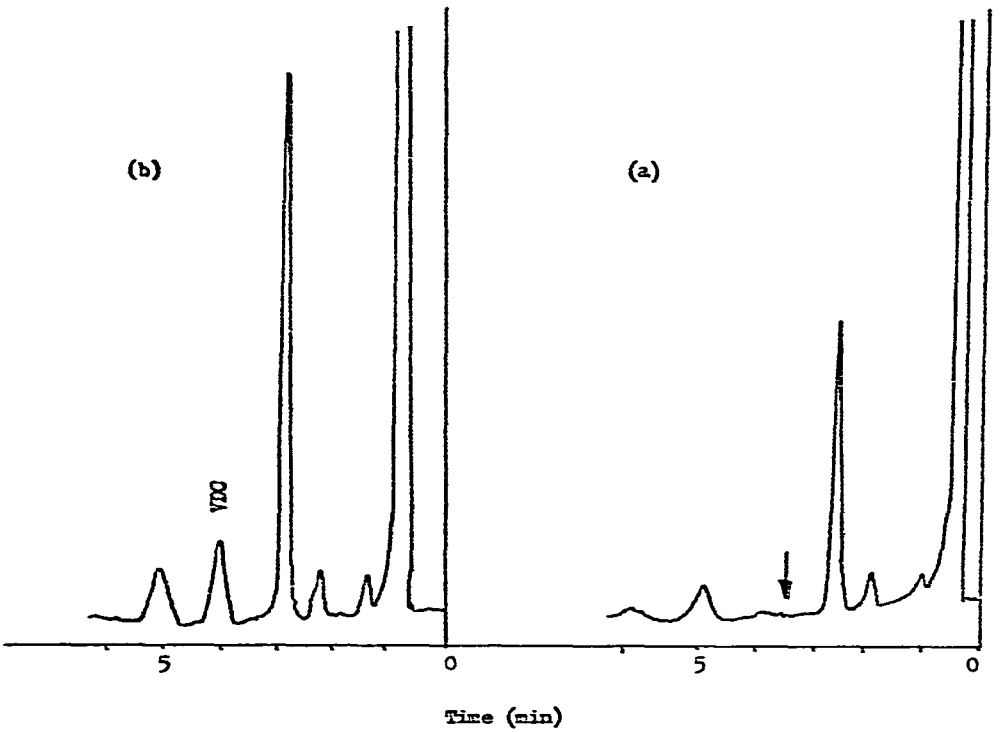

Fig. 3. Headspace chromatograms from above (a) potato crisps which had not been in contact with plastic packaging; (b) potato crisps packaged in PVDC-coated polypropylene bags (see Table II). Column 2.7 m × 0.2 cm I.D. packed with 80–100 mesh Porasil D, flow-rate 20 ml/min, temperature isothermal at 85°C. ECD operated in pulsed mode at 150 μsec with make-up gas of 60 ml/min (attenuation $2 \cdot 10^2$).

ambient temperature. Once again the decrease in VDC in the bags on storage confirms the data shown in Fig. 2; in this case VDC decreases from 0.022 mg/m² in the unconverted film to 0.003 mg/m² in the bag after 30 days. Levels in the crisps ranged from 0.01–0.025 ppm and are shown in Table II. There was no obvious explanation for the variation in VDC levels in the crisps in the bags.

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