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Short communication

Determination of plasticisers in food by gas chromatography–mass spectrometry with ion-trap mass detection

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Abstract

In this paper a method for the determination of plasticisers in food by gas chromatography–mass spectrometry with ion-trap mass detection is described. The plasticisers were quantified by an internal standard addition method using diisobutyl phthalate as the internal standard. Four selected food samples were spiked with nine different plasticisers at about 0.3 μg/g. The recoveries of the plasticisers were in the range of 90 to 106%. The proposed method shows an improvement in precision and exhibits good linearity over a wide concentration range. The new method was applied to the analysis of real samples and the results were found to agree with those obtained using the well-established isotope dilution technique.

Keywords: Food analysis; Ion-trap mass spectrometry; Plasticisers

1. Introduction

Plasticisers have been used in food contact materials for over 30 years [1]. Despite their long history, the process of assessing the possible health effects arising from their contamination of food began only in recent years, following the studies by the US National Toxicology Program indicating that two common plasticisers (di-2-ethylhexyl phthalate, DEHP, and di-2-ethylhexyl adipate, DEHA) caused carcinogenic effects at high doses in mice and rats of both sexes [2,3]. The implications to humans, however, have yet to be determined. A substantial amount of research effort is thus presently being undertaken world-wide in order to monitor the level of contamination in different types of foods having direct contact with plasticised packaging materials.

Matrix interferences, especially those due to lipids co-extracted from food samples, often make quantitation of plasticisers in foods very difficult even by capillary gas chromatography (GC) with flame ionization detection. Perhaps, GC with mass spectrometric detection is a promising choice to overcome these difficulties [4,5].

In this paper, a new quantitation method based on ion-trap mass detection is proposed for the determination of plasticisers in foodstuffs, where diisobutyl phthalate (DIBP) was used as the internal standard. The precision and dynamic range of the proposed method were determined. The plasticiser levels in some selected food samples and the spiked recoveries were also determined and the results were compared with those obtained using the isotope

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dilution technique, where deuterated analogues were used as internal standards.

2. Experimental

2.1. Instruments and apparatus

The solvent extract was analysed with a Varian 3400 gas chromatograph with a low-background DB-5 capillary column, 30 m×0.23 mm I.D. (J&W Scientific). The oven temperature was set at 100°C for 5 min, then increased to 300°C at a rate of 15°C/min and finally held for 10 min. Helium was used as the carrier gas with the column head pressure set at 9 p.s.i. (1 p.s.i.=6894.76 Pa). The gas chromatograph was equipped with an ion-trap mass detector (Finnigan Magnum GC–MS system, Finnigan MAT, San Jose, CA, USA).

A gel permeation column, 50×2.5 cm I.D., packed with 40 cm height of Bio-Beads SX3 (60–120 μm diameter; Bio-Rad, Watford, UK), was used to separate the plasticisers from the lipids co-extracted from fatty foods prior to GC determination.

All glassware had to be rinsed thoroughly twice with distilled dichloromethane before use in order to avoid cross-contamination.

2.2. Reagents and materials

The plasticiser standards were obtained from TCI Chemical (Tokyo Kasei). Solvents used in the extraction were all of analytical grade. The solvents were distilled and tested plasticiser-free before use. Food samples for the survey of plasticisers in foodstuffs were bought from supermarkets. [2,2,5,5-^{2}H]Adipic acid and [3,4,5,6-^{2}H]phthalic acid for the synthesis of deuterated internal standards were obtained from C/D/N Isotopes. The deuterated analogues were synthesised according to the procedure described by Castle et al. [5].

Table 2
Precision data for the proposed method

Plasticiser	R.S.D. (%)
DEHA	7.6
DOAZ	9.5
ATBC	5.5
BBP	3.6
DBP	4.4
DCHP	7.0
DEHP	7.5
DPOP	4.9
DBS	2.9
Average	5.9

2.3. Procedure

2.3.1. Precision test

A mixed plasticisers standard, 10 mg/l containing DIBP as the internal standard, was prepared (Table 1). A bread sample was spiked with 1 ml of the mixed standard solution and the plasticisers were then determined according to the procedure de-

Table 1
Concentration of the components in the mixed plasticisers standard solution

Plasticiser	Abbreviation	Concentration (mg/l)
Di-(2-ethylhexyl) adipate	DEHA	11.2
Diisobutyl adipate	DIBA	10.0
Di-*n*-octyl azelate	DOAZ	11.8
Tributyl-O-acetyl citrate	ATBC	10.1
Benzyl-*n*-butyl phthalate	BBP	10.5
Di-*n*-butyl phthalate	DBP	11.2
Dicyclohexyl phthalate	DCHP	10.9
Diethyl phthalate	DEP	12.6
Di-(2-ethylhexyl) phthalate	DEHP	10.1
Diisobutyl phthalate	DIBP	12.1
Diphenyl-(2-ethylhexyl) phosphate	DPOP	10.3
Di-*n*-butyl sebacate	DBS	11.9
Di-*n*-octyl sebacate	DOS	11.0

scribed below. A sample blank was also analysed in parallel. The above procedure was repeated for the other four samples. The relative standard deviation was calculated for each plasticiser standard to check the precision of the method.

2.3.2. Dynamic range

The dynamic range, slope and correlation coefficient of the calibration graph were determined for each plasticiser based on the base peak area ratio of the respective plasticiser over a range of concentrations to that of the internal standard. The base peaks selected for different plasticisers are: phthalates (m/z 149); adipates (m/z 129); sebacates (m/z 185); ATBC (m/z 185); DPOP (m/z 251) and DOAZ (m/z 171) (see Table 1 for abbreviations).

2.3.3. Real sample analysis and recovery studies

Three different food samples, gummy candy, egg custard roll and bacon biscuits, were all found to be packed with packaging materials having high levels of plasticisers. The plasticisers in foodstuff were extracted according to the procedure described below. For the recovery studies, 1 ml of the mixed plasticisers standard (about 10 mg/l in each plasticiser) was spiked into four different types of foods, jelly candy, bacon, biscuit and cheese.

For non-fatty foods (such as jelly and candy) about 30 g of the homogenized sample was weighed accurately and put in a 250-ml conical flask. The surface area of the sample in contact with the wrapping film was estimated. Any residue of sweet or candy stuck to the wrapping film was dissolved and washed into the conical flask with several millilitres of water. A 1-ml volume of the internal standard and distilled water (making a total of 100 ml) were added to the sample. The mixture was then shaken with 20 ml of cyclohexane–dichloromethane (1:1) for 2 h with an automatic shaker operated at 150 rpm. The extract was dried over anhydrous sodium sulfate and was then ready for GC–MS determination.

For fatty foods (such as bacon and cheese) about 30 g of the homogenized sample were weighed and put in a 250-ml conical flask. A 1-ml volume of the working internal standard and 50 ml of cyclohexane–dichloromethane (1:1) were added to the sample. The mixture was then shaken for 2 h by an automatic shaker operated at 150 rpm. A 5-ml volume of the extract were taken and dried with anhydrous sodium sulfate. The solvent was then removed by heating gently on a hot-plate and the residue was redissolved in 2 ml of dichloromethane–cyclohexane (1:1) followed by the gel-permeation chromatographic clean-

Table 4
Recovery data for four different types of food samples

Plasticiser	Recovery (%)			
	Jelly	Bacon	Cheese	Biscuit
DEHA	106	100	102	96
DOAZ	99	93	96	90
ATBC	94	102	100	97
BBP	95	97	99	95
DBP	96	105	94	97
DCHP	95	102	97	97
DEHP	97	95	99	98
DPOP	93	105	105	101
DBS	100	105	101	99

Table 3
Data for the calibration graphs for the plasticisers

Plasticiser	Concentration range (mg/l)	Slope (mg/l per unit ratio)	Correlation coefficient
DEHA	0.002–25	17.0	0.9998
DIBA	0.002–25	21.4	0.9994
ATBC	0.002–25	19.6	0.9999
BBP	0.002–25	24.2	0.9996
DBP	0.005–25	9.4	0.9984
DCHP	0.002–25	12.9	0.9999
DEP	0.005–25	14.0	0.9994
DEHP	0.002–25	15.1	0.9999
DPOP	0.002–25	16.3	0.9997
DBS	0.002–25	20.9	0.9998
DOS	0.002–25	13.3	0.9992

Table 5
Nature and plasticiser levels in the packaging materials for selected food samples

Food sample	Nature of packaging	Plasticiser found	Plasticiser level ($\mu g/dm^2$)
Gummy candy	Polypropylene	DBP	840
Egg custard roll	Poly(vinyl chloride) co-polymer	DEHA	49 000
Bacon biscuit	Cellulose acetate	BBP	940
		DBP	900
		DCHP	970

up procedure. The first 90 ml of the eluent were discarded and the following 40 ml of eluent were collected. The eluent was evaporated to 2 ml by heating gently on a hot-plate and was then ready for GC–MS determination.

3. Results and discussion

In 1983, the ion-trap detector was introduced by Finnigan MAT [6] and used as an economical detector for GC [7]. The principles and applications of ion-trap detectors have been discussed by March [8].

Ion-trap mass detection can enable determination of the plasticisers in foodstuffs without using any deuterated analogue as internal standards and hence the proposed method is simpler and more efficient. The precision, dynamic range and accuracy of the proposed method were checked to assess the usefulness of the proposed method.

3.1. Precision test

Having an average relative standard deviation of 5.9% (Table 2) the proposed method did show a great improvement over the method using a conventional quadruple mass spectrometer, where a value of 16% had been reported previously for the determination of plasticisers [4].

3.2. Dynamic range

The dynamic range, as well as the slope and the correlation coefficient of the calibration graph for each plasticiser under study are summarised in Table 3.

Apparently, the determination gives results with good linearity at low plasticiser levels.

3.3. Recovery studies

The four spiked food samples, as well as the sample blanks were analysed. The results are summarized in Table 4.

3.4. Real sample analysis

The nature of the packaging materials used in the selected food samples was identified by infrared spectroscopy and the amounts of each plasticiser in the packaging materials were determined by GC. The results are summarized in Table 5. The plasticiser levels in the selected food samples were determined using ion-trap detection, as well as by the isotope dilution technique (results shown in Table 6).

Table 6
Determination of plasticisers in food samples by two different techniques

Food sample	Storage time/temperature	Plasticiser	Amount of plasticiser ($\mu g/dm^2$)	
			Ion-trap detection	Isotope dilution
Gummy candy	3 months/25°C	DBP	155	149
Egg custard roll	3 days/4°C	DEHA	101	102
Bacon biscuit	3 months/25°C	BBP	99	92
		DBP	360	366
		DCHP	220	248

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