Asian Journal of Chemistry; Vol. 27, No. 4 (2015), 1375-1380

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17986

Determination of 16 Phthalic Acid Esters in Medical Infusion Plastic Bottles by GC-MS

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Received: 12 May 2014; *Accepted*: 28 July 2014; *Published online*: 4 February 2015; AJC-16796

To establish a gas chromatograph mass spectrometer method for the determination of 16 phthalic acid esters (PAEs) in medical infusion plastic bottles. Sample pretreatment procedures involved of dichloromethane as extraction solvent and ultrasonic extraction method. There was a good linearity range of related 16 phthalic acid esters was observed. The correlation coefficient was ranged at 0.9907-0.9998. Low detection limits of 0.02-0.09 μg g^{-1}. The mean recoveries were in the range from 82.3 to 101.6 % at 8 and 1 μg g^{-1} spiked levels and the relative standard deviations were in the range of 1.12 and 4.86 % (n = 6). Meanwhile, phthalic acid esters were determined in 40 medical infusion plastic bottles from four pharmaceutical companies in Bengbu city of Anhui province of China. The survey of 40 samples showed dimethyl phthalate, diisobuthyl phthalate and dicyclohexyl phthalate had 100 % (40:40), 87.5 % (35:40) and 45 % (18:40) detection rate. The dimethyl phthalate, diisobuthyl phthalate and dicyclohexyl phthalate were detected at the range of 0.06-0.6 μg g^{-1}, which indicated that more attention should be paid to the phthalic acid esters in medical infusion plastic bottles.

Keywords: Medical infusion plastic bottles, Phthalate acid ester, GC-MS.

INTRODUCTION

Polypropylene (PP) is a thermoplastic resin made from polymerized acrylic monomers. At present, it is widely used in the preparation of medical infusion bottles in China and statistical data reveals, infusion bottles containing polypropylene account for 80 % market in the transfusion industry[1]. Compared with infusion bottles without polypropylene, using polypropylene as materials can has reduce their cost and make a greater profit. However, the result of *in vitro* study by using a roboticized MCF-7 cell proliferation assay revealed that polypropylene products displayed estrogenic properties, so it is worth studying whether add phthalic acid esters (PAEs) in the process of preparing polypropylene plastic[2].

Phthalic acid esters (PAEs), also known as phthalate environmental hormones compounds. They are substances with a diester structure, containing a benzene ring with two ester functional groups[3]. Phthalic acid esters were defined as endocrine disruptors by the world health organization (WHO). In the process of plastic production, phthalic acid esters are additives that are used plasticizers for polymers such as polyvinyl chloride, polyethylene and polyvinyl acetates and so on[4], primarily to improve their flexibility, extensibility, elasticity and workability[5,6].

Phthalic acid esters have attracted wide attention because that these substances can be accumulated and have potential toxic, which can cause disruptions in nervous and endocrine systems, increase risk of cancer, reduce fertility, *etc*[7]. Public safety concerns about human exposure to phthalates are on the rise.

Up to date, many quantitative methods based mainly on gas chromatograph (GC) with flame ionization detector (FID), gas chromatograph mass spectrometer (GC-MS) and high-performance liquid chromatography mass spectrometer (HPLC) have been proposed for phthalates determination[8]. Several analytical methods have been developed for determining phthalic acid esters in water, in wine, in vegetable oil and in food packaging bags, However, correlation study of phthalic acid esters in medical infusion plastic bottles has not been well described.

The aim of this study, was to develop an analytical procedure to detect and quantify the 16 phthalate levels in medical infusion plastic bottles. Particularly, this is necessary for the choice of solvent extraction and the optimization of extraction method[9]. By a combination of dichloromethane as extraction solvent and ultrasonic extraction, the phthalic acid esters in medical infusion plastic bottle samples were analyzed by gas chromatograph mass spectrometer. Besides, we aimed to survey the medical infusion plastic bottles quantification of phthalic acid esters in pharmaceutical companies in Bengbu city of Anhui province[10].

EXPERIMENTAL

A standard of 16 phthalic acid esters mixture in *n*-hexane, dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), di-*n*-butyl phthalate (DBP), *bis*(2-methoxyethyl) phthalate (BMEP), *bis*(4-methyl-2-pentyl) phthalate (BMPP), *bis*(2-ethoxyethyl) phthalate (BEEP), diamyl phthalate (DPP), di-*n*-hexyl phthalate (DHXP), butylbenzyl phthalate (BBP), *bis*-2-buthoxyethyl phthalate (DBEP), dicyclohexyl phthalate (DCHP), di(2-ethylhexyl) phthalate (DEHP), diphenyl phthalate (DPhP), di-*n*-octylo-phthalate (DNOP), dinonyl phthalate (DNP), 1000 mg L^{-1} were purchased from Dikma Co. (Beijing, China). DMP, DIBP and DCHP standards were purchased form Dikma Co. (Beijing, China). Water was purified by a Milli-Q SP system. *n*-Hexane, dichloromethane, acetone and alcohol were all HPLC-graded and purchased from Merck Co. (Darmstadt, Germany).

Standard preparation: Stock solutions of each phthalic acid esters (1000 μg mL^{-1}) were prepared with HPLC grade *n*-hexane and stored in a refrigerator at 5 °C. Working solutions were prepared by diluting stock solutions with *n*-hexane. Sixteen phthalic acid esters standard compounds were diluted to 10 μg mL^{-1}, then draw the standard compounds (10 μg mL^{-1}) 8, 4, 2, 1, 0.5 to 10 mL volumetric flask and diluted with hexane as reference solution of 8, 4, 2, 1, 0.5 μg mL^{-1}. All solvents and solutions for GC-MS analysis were filtered through a Millipore filter (pore size 0.22 μm)[11].

Apparatus and procedures: The chromatographic instrument was 7890A GC-5975C MS (Agilent) High Performance Gas Chromatograph Mass Spectrometer with an EI detector and an automatic injector. Analytes were separated on an HP-5MS (30 m × 0.25 mm × 0.25 μm) gas chromatographic column. The inlet was set at 250 °C and automatic injections of 1 μL of extracts were performed in a splitless mode. The helium carrier gas (purity ≥ 99.999 %) flow was set at 1 mL min^{-1} [12]. The oven temperature programme began at 60 °C and it was increased to 180 °C at a rate of 20 °C min^{-1} with 1 min hold time and a second ramp to 290 °C at a rate of 5 °C min^{-1} with 6 min hold time. The GC-MS interface was set at 280 °C. Scan acquisition in positive chemical ionization was from *m/z* 50 up to 650 a.m.u. The MS detection was in selective ion monitoring operating mode (SIM) at an electron impact energy of 70 eV [9]. Two or three mass fragments were selected for each compound. The most intense ion was used for quantification and the other ions were used for confirmation the presence of the compounds. Transfer line temperature and ion source temperature were maintained at 280 and 230 °C[13]. Solvent delay 8.2 min

Glassware and reagent control: Due to the ubiquitous presence of phthalic acid esters in the environment and samples, the analysis of these compounds was complicated by the lack of appropriate blanks. To avoid phthalic acid esters contamination, glassware had been used instead of plastainer and that had been washed by ultrapure water for three times, then soaked in the acetone for 30 min and dried at 200 °C for 2 h[14]. All glassware and reagents were checked for potentially phthalate contamination.

Sample preparation: There are 40 batch medical infusion plastic bottles from four different manufacturers of Bengbu city Anhui province, China. In phthalate analysis special attention has to be given to sources of contamination. All the glassware should be washed carefully to avoid contamination. Weighed 2 g (exact weight to ± 0.001 g recorded) blending medical infusion plastic bottle samples that were cut up 2 mm width and 2 cm length, then add the chromatographic pure 25 mL dichloromethane, ultrasonic extraction 0.5 h, take supernatant on millipore filter (0.22 μm) for GC-MS analysis. The method is simple, high extraction efficiency, less impurity interference[15].

Blank controls: Evaluating and monitoring of blank values allow the estimation of the mean value of the blank value as well as the corresponding standard deviation. A variety of different sources, such as matrices, reagent and any residual bias in the measurement device or process, will potentially contribute to the blank values of phthalic acid esters. Therefore they need to be well controlled, so add the chromatographic pure dichloromethane 25 mL to glass tube without the samples, ultrasonic extraction 0.5 h, take supernatant on Millipore filter (0.22 μm) for GC-MS analysis[8].

RESULTS AND DISCUSSION

Choice of extraction solvent: Phthalic acid ester compounds are fat-soluble compounds, soluble in many organic solvents, so use dichloromethane, *n*-hexane, ethanol, methanol and tetrahydrofuran solvent extracting the sample, but as strong polar solvent, ethanol and methanol have damage effect on the gas chromatographic column, which may increase the column loss and reduce the service life of the pillars. Tetrahydrofuran solubility is good, but due to its volatile, poor stability and the residue can blocked capillary column easily after the sample dissolved, the column loss serious. Therefore, we mainly investigate dichloromethane and *n*-hexane extraction effect.

Weighed 2 g blending medical infusion plastic bottle samples and cut into 2 mm width, 2 cm length, then the one join the chromatographic 25 mL pure dichloromethane, the other one add the chromatographic pure *n*-hexane 25 mL, ultrasonic extraction 0.5 h, take supernatant on Millipore filter (0.22 μm) for GC-MS analysis. We found that using dichloromethane as extraction solvent had a better efficiency than *n*-hexane. The chromatograms of *n*-hexane and dichloromethane extraction liquid were shown in Figs. 1 and 2, the extraction efficiency of the two liquid was shown in Fig. 3.

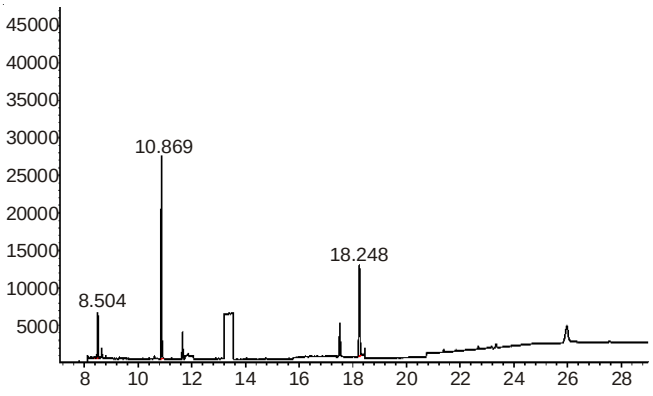

Fig. 1. *n*-Hexane extract SIM chromatograms

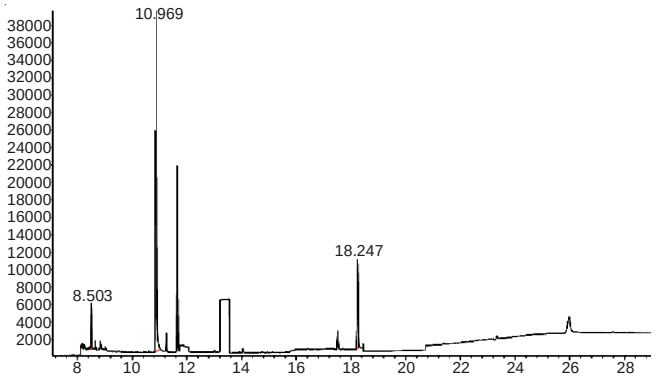

Fig. 2. Dichloromethane extract SIM chromatograms

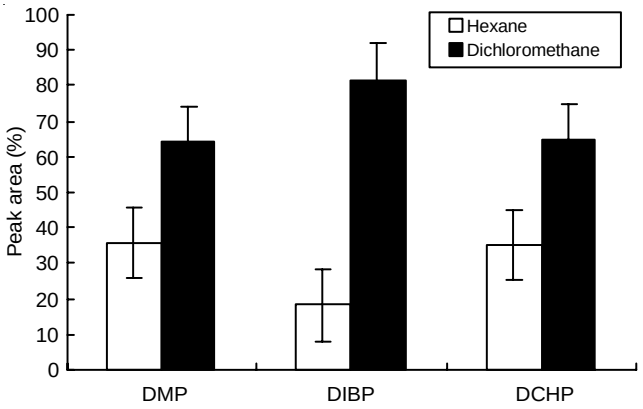

Fig. 3. Two kinds of solvent extraction efficiency

Choice of extraction method: For the polypropylene medical infusion plastic bottles, the common pretreatment methods were Soxhlet extraction, ultrasonic extraction and oscillation extraction. Weighed 2 g blending medical infusion plastic bottle samples and applied soxhlet extraction (90 °C water bath for 6 h), ultrasonic extraction (extraction time 0.5 h), oscillation extraction (extraction time 1 h) extracting the samples. In the case of dimethyl phthalate (DMP), diisobutyl phthalate (DIBP), dicyclohexyl phthalate (DCHP) content in the samples, when we used ultrasonic extraction extracting samples, the DMP, DIBP, DCHP recoveries were higher than that of the other methods, otherwise, ultrasonic extraction method was simple and had little pollution to the environment. For the above considerations, we chose the ultrasonic extraction to extract samples. The samples extract ion chromatogram was shown in Fig. 4, the sample added standard substance extract ion chromatogram was shown in Fig. 5 and the recoveries result of three extraction methods were included in Table-1.

Extraction optimization: In the experiment, through compared the soxhlet extraction, Ultrasonic extraction, Oscillation extraction, we applied the ultrasonic extraction extract samples. The method was simple and quick, but it is worth considering that the extraction temperature and time[16].

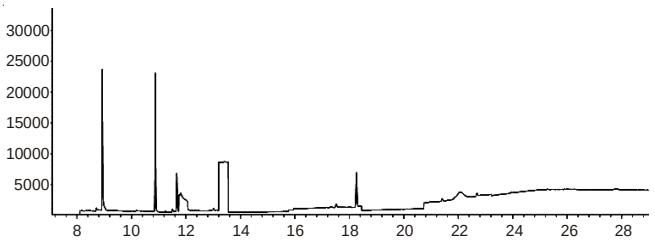
Fig. 4. Chromatogram of DMP, DIBP and DCHP applying GC-SIM-MS in samples

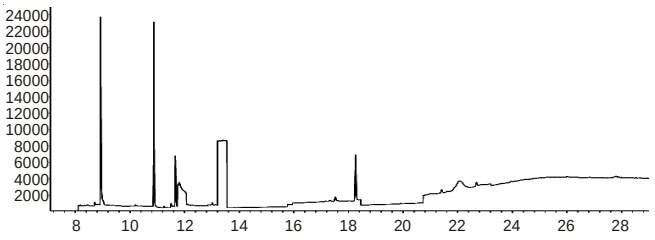
Fig. 5. Chromatogram of DMP, DIBP and DCHP applying GC-SIM-MS in samples which added standard substance

Extraction temperature optimization: We adopt the ultrasonic extraction method to extract the sample 0.5 h on 20, 30, 40, 50 and 60 °C[17]. The result was shown in Fig. 6. With the increase of temperature, the extraction quantity of DIBP, DCHP, DMP was increasing, but when the temperature was higher than 40 °C the extraction quantity of DIBP, DCHP, DMP began to decline. Due to the extracting agent was organic solvent, with the increase of temperature the volatilization of extracting agent was accelerated. When the temperature was higher than 40 °C, the volatilization of extracting agent would lead to the lose of the target. In addition, with the increase of temperature the process of ultrasonic extraction will appear collapse phenomenon which lead to the volatilization of extracting agent, the test error may be increase. In conclusion, the best extraction temperature was 40 °C in this experiment.

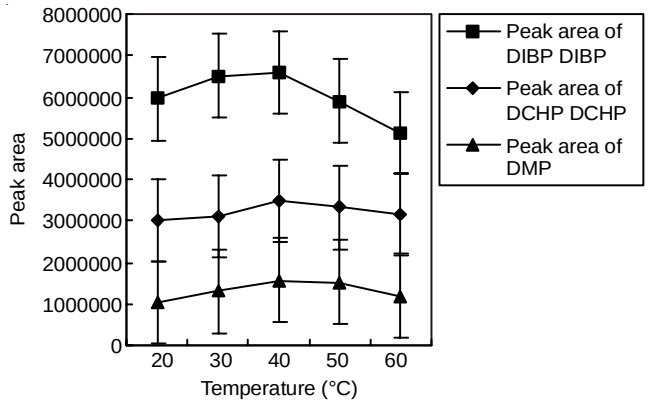

Fig. 6. Influence of temperature on the extraction of DMP, DIBP and DCHP quantity

TABLE-1
RECOVERIES RESULT OF THREE EXTRACTION METHODS

Method	Sample 1			Sample 2		
	DMP (%)	DIBP (%)	DCHP (%)	DMP (%)	DIBP (%)	DCHP (%)
Soxhlet extraction	102.3	99.81	108.24	101.78	100.96	104.3
Ultrasonic extraction	108.7	110.8	106.3	111.7	105.6	106.7
Oscillation extraction	98.74	101.2	97.86	95.75	100.0	97.86

Extraction time optimization: We adopt the ultrasonic extraction method to extract the sample on 40 °C for 10, 20, 30, 40 and 50 min[18]. The result was shown in Fig. 7. As the extension of time. the extraction quantity of DIBP, DCH, DMP was increasing, but when extracting time was more than the enrichment of the saturation point, it was obvious that the extraction quantity of DIBP, DCHP, DMP began to decline after 40 min, so the extraction time was 30 min.

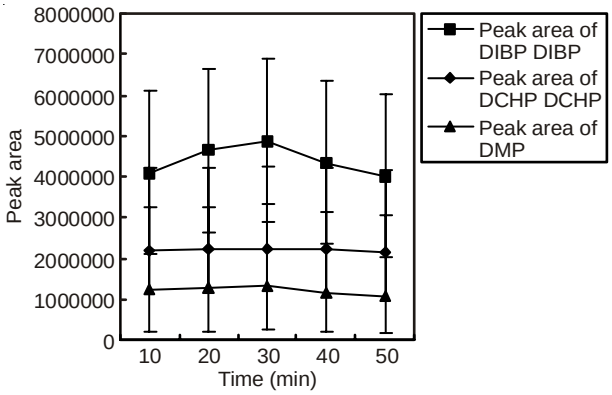

Fig. 7. Influence of time on the extraction of DMP, DIBP and DCHP quantity

Linearity and sensitivity: All the 16 phthalic acid esters in medical infusion plastic bottles samples were analyzed by GC-MS. All 16 phthalates were well separated in less than 25 min without significant interference from the sample matrices. Four fragment ions were monitored for each compound. The most characteristic ion in the chromatography was selected for quantification and the other three ions for the purpose of confirmation[5]. The qualifier ions and quantifier ions and retention time of 16 phthalic acid esters were listed in Table-2. The total ion current chromatograms of the 16 phthalic acid esters were shown in Fig. 8. The linear equations and correlation coefficients of the 16 phthalic acid esters were obtained as in Table-3. All the 16 phthalic acid esters showed good linearity and the correlation coefficients were 0.9907-0.9998. The estimated LOD for each phthalate were determined at a S/N of 3:1, which was 0.02-0.09 μg mL^{-1} and the results were shown in Table-3.

Blank values: Due to the wide spread applications of phthalic acid esters in consumer products, phthalates are commonly found in the laboratory environment and reagents and this is a major issue when developing methods for determination of phthalates[19]. In the reagents, there are always

TABLE-2
OPTIMIZED PARAMETERS FOR ANALYSIS OF 16 PHTHALIC ACID ESTERS

No.	Retention time (min)		Phthalic acid esters	Ion pair (*m/z*)
	4 (μg mL^{-1})	1 (μg mL^{-1})		
1	8.249	8. 231	DMP	163, 133, 77, 76
2	9.092	9.011	DEP	149, 104, 191, 65
3	10.968	10.966	DIBP	105, 207, 91, 77
4	11.765	11.627	DBP	149, 207, 56, 57
5	12.117	12.110	DMEP	149, 207, 150, 56
6	12.850	12.714	BMPP	104, 76, 56, 57
7	13.245	13.215	DEEP	149, 207, 72, 73
8	13.637	13.632	DPP	149, 150, 148, 55
9	15.852	15.947	DHXP	149, 207, 150, 55
10	16.018	16.135	BBP	149, 206, 91, 65
11	17.485	17.520	DBEP	56, 57, 85, 101
12	18.187	18.274	DCHP	149, 167, 56, 55
13	18.401	18.552	DEHP	149, 167, 279
14	18.547	18.643	DPhP	225, 104, 76, 77
15	20.810	20.978	DNOP	149, 150, 279
16	23.444	23.514	DNP	149, 71, 57

TABLE-3
REGRESSION EQUATION, CORRELATION COEFFICIENT, AND LOWEST DETECTION LEVEL OF THE 16 PHTHALIC ACID ESTERS

No	Phthalic acid esters	Linear eq	Correlation coeff. (r)	LOD (μg g^{-1})
1	DMP	$Y = 2.3 \times 10^6X - 4.8 \times 10^5$	0.9998	0.04
2	DEP	$Y = 2.9 \times 10^6X - 8 \times 10^5$	0.9996	0.02
3	DIBP	$Y = 3.2 \times 10^6X - 6.3 \times 10^5$	0.9945	0.01
4	DBP	$Y = 3.3 \times 10^6X - 1.3 \times 10^6$	0.9974	0.05
5	DMEP	$Y = 1.7 \times 10^6X - 1.2 \times 10^6$	0.9941	0.08
6	DMPP	$Y = 2.8 \times 10^6X - 1.5 \times 10^6$	0.9971	0.02
7	DEEP	$Y = 2.2 \times 10^6X - 1.6 \times 10^6$	0.9950	0.09
8	DPP	$Y = 3.4 \times 10^6X - 1.7 \times 10^6$	0.9985	0.05
9	DHXP	$Y = 2.9 \times 10^6X - 2.2 \times 10^6$	0.9907	0.06
10	BBP	$Y = 2.8 \times 10^6X - 1.8 \times 10^6$	0.9961	0.05
11	DBEP	$Y = 5.3 \times 10^5X - 1.8 \times 10^5$	0.9979	0.08
12	DCHP	$Y = 2.6 \times 106X - 1.7 \times 10^6$	0.9944	0.03
11	DEHP	$Y = 3.1 \times 10^6X - 1.8 \times 10^6$	0.9949	0.02
12	DPhP	$Y = 3.0 \times 10^6X - 1.4 \times 10^6$	0.9967	0.05
15	DNOP	$Y = 2.1 \times 10^6X - 1.4 \times 10^6$	0.9971	0.02
16	DNP	$Y = 3.0 \times 10^6X - 91596$	0.9967	0.08

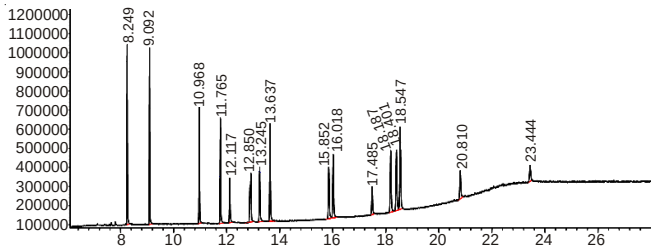

Fig. 8. Total ion current chromatograms of the 16 phthalic acid esters

contaminations of phthalic acid esters, such as DMP, DEHP and DBP, *etc*. The most significant influence of the blank values is the dichloromethane used in the liquid extraction in this work. In order to know the concentrations of the phthalic acid esters in the HPLC-grade dichloromethane, we used in the SPE process, the total ion current chromatograms HPLC-grade dichloromethane was analyzed and shown in Fig. 9 in which the concentrations of phthalic acid esters are lower than 0.001 g mL^{-1}, whose influences can be ignored[9].

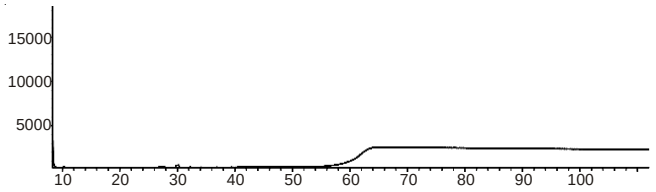

Fig. 9. Total ion current chromatograms HPLC-grade dichloromethane

Accuracy and stability: Accuracy was estimated through recovery experiments by spiking blank sample (n = 6). The experiments were conducted at high (8 μg g^{-1}) and low (1 μg g^{-1}) levels of 16 phthalic acid esters, respectively. The medical infusion plastic bottle samples were followed by ultrasonic extraction, GC-MS analysis[9]. The recovery and RSD were given in Table-4. The date showed that the recovery for the 16 phthalic acid esters were in the range of 90.56 to 104.36 % for all phthalates with a RSD value from 1.21 to 5.12 %.

Method stability studies were performed by injecting the sample added standard substance which stored 2, 4, 6, 8, 10 h at the normal temperature[20]. The amount of sixteen phthalic acid esters RSD were below 2 %.

In this study, a ultrasonic extraction methods and GC-MS were developed for the simultaneous determination of 16 phthalic acid esters of in 40 medical infusion plastic bottles. The method was validated by its linearity, precision, accuracy and stability. It is an important criterion for a high efficiency GC-MS condition that the mark peaks have greatly baseline separation with adjacent peaks within a short analysis time as far as possible. In the process of pretreatment of samples, we compared the different extraction solvent and determined the dichloromethane as extraction solvent, then we compared the recoveries of soxhlet extraction, ultrasonic extraction and oscillation extraction for DMP, DIBP, DCHP and discovered the ultrasonic extraction had a high recovery rate. The pretreatment of samples methods were simple, fast and little pollution to environment. In order to make the sample of the phthalic acid esters can be fully extracted, We optimized the ultrasonic extraction of the extraction time and extraction temperature, we discovered when the extraction time was 0.5 h and extraction temperature was 40 °C, the extraction quantity of DIBP, DCHP, DMP were highest.

The analytical procedure reported was applied to 40 medical infusion plastic bottles. All the samples were collected form the pharmaceutical companies in bengbu city of Anhui province. In 40 medical infusion plastic bottles form Bengbu, DMP, DIBP and DCHP were detected at the range of 0.06-0.63 μg g^{-1}. The detection rates were 100 % (40:40), 87.5 % (35:40) and 45 % (18:40). Other 13 phthalic acid esters were not detected[3]. Dimethyl phthalate was found in all samples in a range from 0.06 to 0.36 μg g^{-1}. Diisobutyl phthalate was found in 35 samples in a range from 0.12 to 1.13 μg g^{-1} and dicyclohexyl phthalate with the level of 0.10 to 0.63 μg g^{-1}.

Conclusion

Based on the chemical properties of phthalic acid esters, we compared two different extraction solvents and three extraction methods, the result showed when dichloromethane was used as solvent and applied ultrasonic extraction to pre-treat the samples, high extraction efficiency was gained, the recovery rate of 16 phthalic acid esters was high. In the experiment, we optimize the extraction temperature and time, in the end, we

TABLE-4
RECOVERIES OF 16 PHTHALIC ACID ESTERS IN MEDICAL INFUSION PLASTIC BOTTLES

No.	Phthalic acid esters	Added 8 (μg g^{1})		Added 1 (μg g^{1})	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
1	DMP	102.4	1.21	100.3	2.41
2	DEP	101.7	1.56	99.92	3.14
3	DIBP	98.58	2.15	97.55	4.02
4	DBP	104.36	2.46	102.34	3.78
5	DMEP	97.66	3.55	99.43	4.32
6	DMPP	93.82	2.68	92.78	5.02
7	DEEP	95.14	1.98	97.12	4.36
8	DPP	96.50	3.96	98.23	5.10
9	DHXP	92.98	4.21	93.45	4.33
10	BBP	100.34	3.44	101.52	3.67
11	DBEP	90.56	2.59	94.97	5.12
12	DCHP	96.32	4.68	95.03	4.78
13	DEHP	101.87	4.21	97.50	3.99
14	DPhP	97.12	2.43	98.79	2.88
15	DNOP	102.68	4.62	100.03	4.09
16	DNP	94.67	2.34	95.85	3.98

chose 40 °C and 0.5 h as the best extraction temperature and time. The survey of 40 medical infusion plastic bottles samples showed DMP, DIBP and DCHP had the 100 % (40:40), 87.5 % (35:40) and 45 % (18:40) detection rate. Therefore, more attention should be paid to the phthalic acid esters in medical infusion plastic bottles.

ACKNOWLEDGEMENTS

The authors thank De-Zhou Ge and Hao Liu for their help during the experiment. This work is funded by The National Natural Science Foundation of China (81000992, 81072207) and Bengbu Medical College Graduate Student Research Innovation Project (Number: Byycx1330)

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