ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 11, No. 1 (2010) 66–72

Assay of Aliphatic Phthalates in Polymer Products by Sensitive Polarographic Method: Health and Environmental Issue

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Abstract

A faster, simpler and sensitive method was developed for determination of aliphatic phthalates using differential pulse polarography (DPP) as standard technique. The choice and concentration of base electrolyte, solvent, initial potential, effect of water addition and interference by other phthalates were the main parameters to optimize for enhancement of peak current and to obtain well-defined polarogram with lower background current using 1.3×10^{-4} M di-butyl phthalate (DBP) solution. Best results were obtained in the presence of tetra methyl ammonium bromide (TMAB) as electrolyte in methanol solvent with initial potential, -1.4 V. A linear calibration plot was observed in the range of $3 \times 10^{-7} – 1.6 \times 10^{-4}$ M DBP solution as aliphatic phthalates with lower detection limit of 5.9×10^{-8} M and linear regression coefficient of 0.9987. The developed polarographic method was successfully applied for analysis of aliphtaic phthalates in various samples of locally available polymer products such as baby toys, nipples, teethers, infusion blood bags and shopping bags. The results of the current method were compared with those obtained by a reported method and good agreement was found between them.

Keywords: phthalates; Differential pulse polarography; Polymer products; Comparative method.

Introduction

The dialkyl or alkylarylesters of 1, 2-benzenedicarboxylic acid are commonly called phthalates [1]. Phthalates are widely used for production of several industrial and household products and thus found in plastic products such as lubricants, baby toys and infant care products, chemical stabilizers in personal care products, cosmetics, and polyvinyl chloride tubing. Due to non-chemical attachment of these compounds to the final products, they are continuously released into air or leached into liquids by various routes [2].

Phthalates including dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, di-(2-ethylhexyl) phthalate (DEHP) and di-n-octyl phthalate (DnOP) are well known plasticizers and are omnipresent in the environment [3]. In the recent years, much attention has been focused on phthalates exposure due to the suspicion of their carcinogenic and estrogenic properties. Due to their widespread use, relatively large quantities are released into the environment and the evaluation of these compounds in different samples is thus essential for environmental risk assessment [4].

Determination of phthalates is carried out by various methods such as micellar electro kinetic chromatography (MEKC) [4], gas chromatography GC [5–7], gas chromatography-mass spectroscopy

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(GC-MS) [8, 9], high performance liquid chromatography (HPLC) [1, 10, 11], atomic absorption spectroscopy (AAS) [12] and electroanalytical methods [13, 14].

Some researchers [13] used the extraction of phthalates from sample with ether followed by its evaporation and re-dissolution in methanol. Moreover, they employed cathodic-ray polarograph which is far more inferior to the current technique of DPP concerning the improved calibration range and lower detection limits in the later case. Tanaka and Takeshita [14] used DPP but the additional steps such as using different chemicals for extraction, hydrolysis, etc. before polarography which makes the process not only complicated but expensive as well. Moreover, their working range was narrower and limit of detection higher due to use of non specific electrolyte.

The current work was carried out to develop a faster, simpler and economical DPP method by avoiding extra chemicals and additional steps. The main attention was focused on looking for an appropriate electrolyte and solvent system which could improve the calibration range and lower the detection limit as compared to previously reported electrochemical method [14] for determining phthalates. Further objective was the application of the developed method for assaying phthalates in samples of various polymer products.

Experimental

Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade obtained from Merck, Fluka and BDH chemicals with greater than 99% purity. All glassware was cleaned by dipping in 3 M HNO_3 solution overnight and then thoroughly washed with detergent water followed by tape water and finally rinsed by using doubly distilled water. The glassware was then dried in an oven at 110 ^{0}C until complete dryness and cooled to room temperature before use. Stock solution of 0.1 M DBP was prepared in pure methanol. Dilute working standards were prepared from this solution in methanol after adding appropriate quantity of electrolyte.

Apparatus

Trace analyzer model 797 of Metrohm Version 1.1 was the main instrument employed for polarographic analysis of phthalates. The cell consisted of three electrodes with saturated calomel as reference, platinum wire as counter and dropping mercury as working electrode. Model 7000A GC/MS of Agilent Technologies was used for comparative analysis of aliphatic phthalates (as phthalic acid) in samples.

Analytical procedure

According to polarographic procedure, 10 mL blank solution containing 0.1 M electrolyte (taken as 1 mL from 1 M stock solution prepared in methanol) was first run by DPP method at optimized conditions in order to get a background polarogram in the potential range of -1.4–1.9 V. The optimized conditions included, pulse amplitude, 0.05V, pulse time, 0.4sec, voltage step, 0.06V, voltage step time, 0.00595 s, and surface area, 0.15mm^2 DME. Standard solution containing 1.3×10^{-4} M DBP and electrolyte was then processed under similar conditions and the differential pulse polarogram of phthalate was observed at a peak potential value of -1.73 V. Calibration plot was thus recorded for a number of DBP standard solutions (considered as aliphatic phthalates). Similar treatment was performed for dilute samples and the unknown concentration of phthalates found from calibration plot of standard phthalates solutions. The actual concentration of phthalates was obtained by multiplying this value with respective dilution factor.

Sample preparation

Phthalates were extracted from various polymer products by Soxhlet extraction method. According to the procedure, 10 g of the sample (small pieces) was taken in a filter paper thimble and placed in Soxhlet tube. Soxhlet tube was fitted to a round bottom flask containing 100 mL of methanol at its lower end and water condenser at upper end. The assembly was placed on heating water bath for two hours at 70–80^{0}C. The extractant was cooled, transferred to 100 ml volumetric flask and adjusted to mark with methanol. Diluted sample was prepared from extractant in methanol along with addition of appropriate amount of electrolyte before DPP analysis.

Results and Discussion

Optimization of parameters

The following parameters were optimized for determining phthalates by taking 1.3 × 10^{-4} M solution of DBP prepared in methanol.

Selection of mode

Various modes of polarography and voltammetry were checked to get enhanced polarograms and voltammograms. DPP proved to be the best amongst all available electrochemical techniques giving enhanced current response for phthalates. DPP has also been used by other workers [14] for determining phthalates.

Selection of best organic solvent

The effects of different organic solvents and their combinations were observed upon the variation of peak height of 1.3×10^{-4} M DBP solution in the presence of 0.01M tetra ethyl ammonium iodide (TEAI) (Table 1). Other parameters included, scan rate, 20 mV s^{-1}, and initial potential, -1.5 V.

Table 1. **Effect of organic solvents ratio on DPP peak current of DBP solution.**

	Solvent system				
	Methanol (Pure)	***Ethanol (Pure)***	***Methanol: ethanol (1:1)***	***Methanol: propanol (1:1)***	***Methanol: butanol (1:1)***
Peak current of DBP solution (nA)	582	560	552	524	490

It follows from the table that pure methanol results in best peak current value for phthalate among all systems studied. This may be due to its greater dissolution capability for DBP as compared to other solvents or solvent system. Williams and Kenyon [13] have also reported methanol as the best solvent for polarographic determination of phthalates.

Selection of best electrolyte

Three electrolytes namely, TEAI, TMAB and tetra butyl ammonium bromide (TBAB) were used to choose the best electrolyte for phthalate response using DPP (Fig. 1).

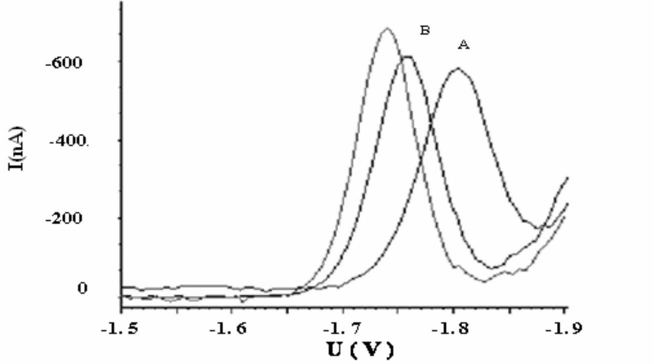

Figure 1. **DP polarograms of 1.3 x 10^{-4}M DBP in the presence of 0.01 M of A) TEAI B) TBAB and C) TMAB.**

It is clear that phthalates show enhanced peak current in the presence of TMAB as compared to other electrolytes. Moreover, the peak potential is shifted towards lower values which results in a sharper and better shaped polarogram. The shift of the peak is also the indication of better interaction of this electrolyte with phthalate. The reason for enhanced current, best shape peak and greater interaction is due to more electronegative nature of bromide ions as compared to iodide ions. Furthermore, the smaller methyl groups have more chance of entering into association with phthalates rather than butyl or ethyl ions. Williams and Kenyon [13] have used tetra methyl ammonium iodide (TMAI) as the electrolyte of choice for determining DBP by cathode-ray polarography in the presence of methanol solvent while Tanaka and Takeshita [14] have used 0.1 M acetic acid/ 0.1 M potassium chloride as electrolyte for determining total phthalates by DPP.

Optimization of concentration of electrolyte

The effect of various concentration of TMAB in the range of 1×10^{-4} – 0.2 M upon the peak current of DBP was studied (Fig. 2). It can be seen that the enhanced peak current for DBP is obtained at an optimum concentration of 1.0×10^{-1} M of electrolyte. The use of TMAI has been cited elsewhere [13] for phthalate analysis by polarography.

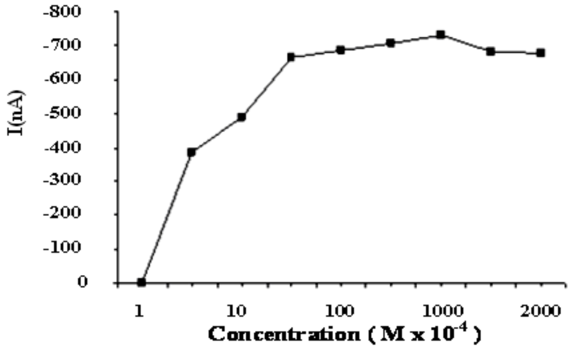

Figure 2. **Effect of concentration of TMAB on the height of the peak current of 1.3 x 10^{-4}M DBP.**

Reversibility/ irreversibility check

Cyclic voltammetry (CV) at HMDE was performed to see the reversibility or irreversibility of the reaction at electrode (Fig. 3).

The results show that the reaction of DBP at mercury electrode is irreversible due to absence of oxidation signal with positive peak current. This shows the analyte is reduced at the electrode surface because negative peak current is indicative of reduction phenomenon. Similar irreversible behavior of phthalates has been cited elsewhere [15]. It is also seen that the CV is not sensitive as compared to DPP regarding the determination of DBP and hence the latter was selected for further studies.

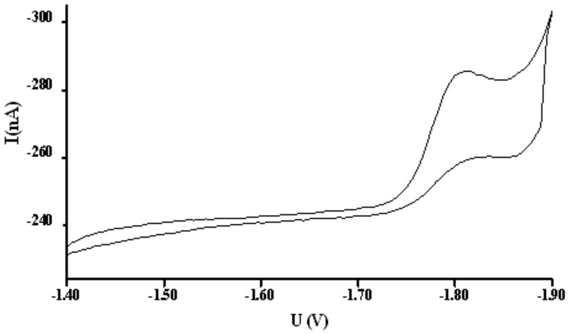

Figure 3. **Cyclic voltammogram of 130 µM DBP in 0.1M TBAB at HMDE at scan rate 100 mVs^{-1}.**

Effect of water addition

The effect of water addition to methanol was studied to verify the applicability of the current method for determining phthalates in aqueous samples. So various combinations of methanol: water system were tried (Fig. 4). It is observed that as the % age of water increases, the peak current decreases in about linear fashion. This effect is due to hydrophobic nature of phthalates [11] in water. It means that phthalates can be determined by polarography at trace level only if present as soluble species in organic solvent.

However, if the aqueous sample containing phthalates is properly dried and dissolved in methanol along with addition of electrolyte then aliphatic phthalates can be determined by current method.

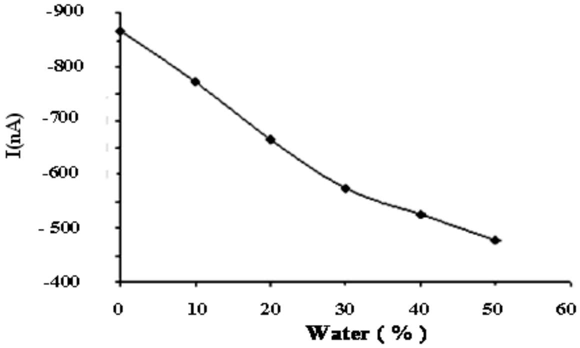

Figure 4. **Dependence of the height of DPP peak of 1.3 x 10^{-4}M DBP on water/ methanol ratio**

Effect of other phthalates (confirmation of process for determination of aliphatic phthalates)

The effect of addition of other phthalates such as dipentyl phthalate, diethyl hexyl phthalate and dioctyl phthalate was studied for the variation in peak current value of DBP. It was observed that each of these phthalates provided a regular increment to the peak current of DBP. It was also confirmed that the peak potentials of these phthalates lay in the range of -1.73 – -1.75 V. This close range of peak potentials of all these phthalates verifies that the current process is not suitable for determining individual phthalates but applicable to all aliphatic phthalates.

Interference by reagents used in polymeric products

DBP and other reagents such as hydroquinone, picric acid, 4-nitrophenol, maleic acid, acryl amide and vinyl chloride (used in polymer product) were mixed in 1:1 ratio in the desired amount of methanolic electrolyte in order to check their interference. The error of 1.5%, -1.2%, 1.8%, 2.2%, -0.8% and 1% was found for the mentioned compounds when mixed and run individually (1:1) with DBP. This proves that the method is valid for application to polymer products.

Calibration plot

A calibration plot was obtained for DBP as a representative of aliphatic phthalates in the range of 0.3–160 µM solution after applying all optimized parameters (Fig. 5). A detection limit of 59 nM was found for phthalates with linear regression coefficient of 0.9987.

The good linearity of the plot confirms the accurate determination of phthalate within the described range. The calibration range and limit of detection (LOD) of our newly developed method for aliphatic phthalates determination are better than that reported [14] where a range of 2–100 µM and LOD of 0.5 µM was described for phthalates using DPP. The current method is also simpler and economical than the previously reported methods [13–14].

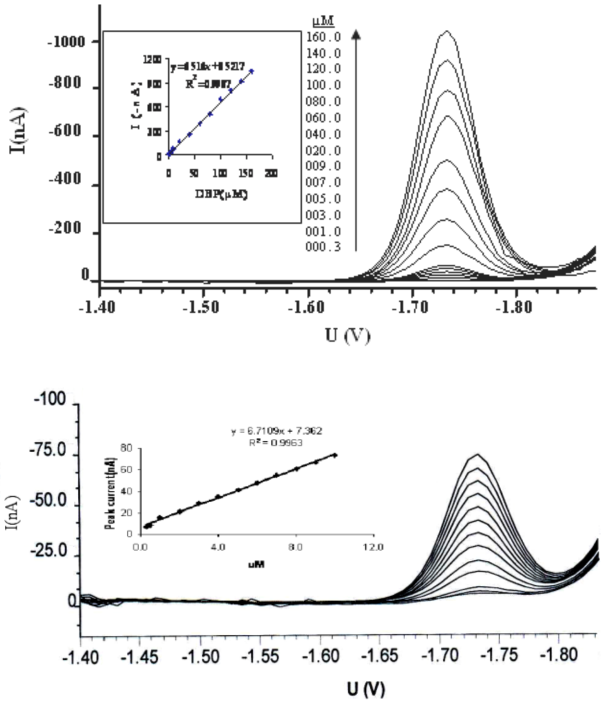

Figure 5. **DPP calibration curve for aliphatic phthalates in the range of a) 0.3–160 µM; b) 0.3– 9 µM. (insets show respective linear plots).**

Validity of method (application to sample analysis)

The developed method was applied to dilute samples of various polymer products after Soxhlet extraction into methanol under optimized parameters. The DP polarograms of 100 times diluted sample of teether (5 replications) are shown (Fig. 6).

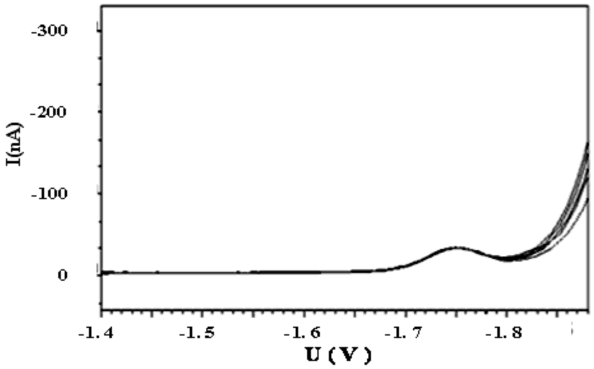

Figure 6. **DPP of 100 fold dilute sample of teether with 5 replications.**

The closeness of replicated polarograms with relative standard deviation of 0.12% reveals a very good reproducibility for the developed method.

The recovery test for a 200 time diluted teether sample was performed (Table 2) in order to fully validate the proposed method for polymer product in the presence of other agents (if any) at their actual existence level.

Table 2. **Phthalates in a 200 times (methanol) diluted sample from teether.**

DBP added (µM)	Found (µM)	Difference (µM)	Recovery (%)
0.0	1.68	1.68	-
1.0	2.66	0.98	98.0
2.0	3.66	1.98	99.0
5.0	6.72	5.04	100.8
10.0	11.50	9.82	98.2

The recovery of DBP as aliphatic phthalates in the range of 98–100.8% reflects the fact that the method is very well suited for application to polymer products and further confirms the negligible interference by other reagents present in polymeric products (see section 3.9).

The results for phthalates found in various types of polymer product samples by this method and those obtained by a reported method [16] are displayed (Table 3). It is clear from the table that the results obtained by two methods are quite close at low concentrations of phthalates. However as the dilution factor decreases and hence the final concentration in the product increases, greater difference in the results are seen. So it means that this method is more valid for lower concentration values. Teether samples contain aliphatic phthalates in the range of 80 – 115 µg/g (0.008–0.012%) in terms of DBP. As the permissible exposure limit (PEL) for phthalates is 5mg / m^3 (0.44 ppm in terms of DBP) [17] so these are still higher values and mirror a problem of great concern regarding the transfer of phthalates by oral routes in the children below 3 years of age. Nipples are another major cause of phthalates toxicity in children. Baby toys are among the highest donors of phthalates toxicity in children as most of the children chew them instead of playing with. The phthalates contents of PVC toys have also been evaluated by other workers [18] who have reported a value of 20% for “bath ducks” using GC/ MS.

Plastic shopping bags are one of the major causes of phthalates toxicity for general public regardless of age as they are utilized by all types of people due to their negligible cost, good strength and light weight.

It is the matter of great concern that the blood bags have the highest concentration of phthalates in the range of 3.2×10^{-5} – 3.58×10^{-5} g/g (34.2–37.4% w/w) followed by baby toys ranging from 1.95×10^{-5} – 2.53×10^{-5} g/g (20.4–26.5% w/w). As blood bags are utilized by various patients during blood transfusion, so there is a great possibility of transfer of these phthalates directly into body. This can result in introduction of some possible carcinogenic and estrogenic problems in the patients. The presence of phthalates in the range of 10–40% has been described in PVC medical products [19]. So the mentioned data (Table 3) presents an alarming situation in terms of much enhanced level of phthalates in the observed and similar products. Sufficient portions of these phthalates released into human bodies [19] and environment by various routes seem to be far higher than PEL value and hence a possible cause of phthalate toxicity. In view of mentioned reports and present observations, it is recommended that the increasing use of shopping bags and other polymer products possessing phthalates must be banned in order to minimize their adverse health impact as well as environmental pollution. Worth mentioning is a signed legislation [20] by the Governor of California in order to protect the health of children by prohibiting the use of phthalates in baby care products and toys designed for children under 3 years of age.

***Table 3.* Phthalates contents in some polymer samples by developed and reported method.**

Sample type	**Sample No.**	**Phthalates (µg/g)[a]**	
		By developed method	***By reported method***
Teether	1	80 ± 0.8	82.7 ± 0.8
	2	90.6 ± 1.0	91.2 ±1.3
	3	115 ± 0.5	114.0 ±1.0
Nipple	1	317 ±5.4	312.0 ± 10.6
	2	346.7 ±5.4	349.2 ± 8.0
	3	370.7±5.4	373.3 ± 10.6
Shopping bag	1	909.3±8.0	906.7 ± 13.3
	2	1008 ±5.4	1008.0 ± 10.6
	3	1045.3±8.0	1042.03 ± 10.6
Baby toy (horse)	1	195466.7±800.0	194666.7 ± 1333.3
Baby toy (camel)	2	208000 ± 1333.0	207466.7 ± 2133.3
Baby toy (rabbit)	3	253600 ±2133.0	252800.0 ± 1866.6
Blood bag	1	328000 ±1600.0	327733.0 ± 2400.0
	2	358400 ± 1066.6	356800.0 ± 1066.6

[a], average of five replications

Conclusion

The newly developed method is simple, economical and rapid for determination aliphatic phthalates not only in polymer products but its use can be extended to other products such as nail polishes, cosmetics, water samples, etc. The method has advantage over other conventional methods for determination of phthalates because of its simpler arrangement, use of inexpensive chemicals in smaller amounts, extended calibration range and lower detection limits. The values of phthalates in various polymer products observed in the above study are far above PEL and it is thus recommended to ban all the products due to their danger in the environments and hence greater health complications.

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