



Gas chromatography-Mass Spectrometric assessment of the presence of phthalates in branded and locally available cosmetics stored in glass and plastic containers

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ABSTRACT

Manmade chemicals belongs to different groups are used in various consumers products as additives. There is threat of high potential of human exposure to daily use of cosmetics. Present analytical investigation was carried out to check the presence of terephthalic acid esters (phthalates) in twenty four (24) locally available and branded samples of nail enamels and moisturizing lotions from market. Comparison among all chosen cosmetics was done to sort best cosmetics used in Pakistan. Gas chromatography – Mass Spectrometric technique was used to determine the presence of phthalates after proper extraction process. It was confirmed that out of twelve samples of nail enamels, seven samples were contaminated with diethyl phthalate (DEP) and remaining contaminated with dibutyl phthalate (DBP). In case of twelve moisturizing lotions, two samples were contaminated with DBP while one was contaminated with DEP. One very important result found in most samples was presence of terephthalic dihydrazide. It is concluded that it may be due to leaching of toxic compound “hydrazine hydrate” from plastic bottles in which they were stored. Comparison of analyzed moisturizing lotions revealed that Nivea and Ponds (moisturizers) are better to use then other analyzed products while none of nail enamels was recommended to use.

Keywords: Phthalates in cosmetics, Phthalates in nail enamels, Phthalates in lotions, Personal care products, endocrine disruptors

INTRODUCTION

Phthalates belong to family of endocrine disruptors the compounds made from alcohols and phthalic anhydride. They are oily, colorless, odorless liquids that do not evaporate readily. Phthalate exposures in the general population and in subpopulations are most common and widely variable. Phthalates are used in variety of products i.e. clothing, pharmaceuticals, cosmetics, children toys, medical devices, food packaging, waxes, insecticides and in many more. If phthalates are used in consumer products then they result in direct human exposure through inhaling or via eye contact and indirectly through leaching or absorption process. In this way they become a source to contaminate the environment [1]. In past, only diet was considered as main source of phthalate exposure in human beings but all its source and pathways are not well understood which contribute to human contact [11]. Metabolite concentrations of phthalates are higher in young children as compared to other age groups [2, 15].

Phthalates are major environmental pollutants and a cause of concern because they are found in most people's blood, tissue, breast milk, and urine. Phthalate esters present in water sample or in faecal samples of living beings known to leach from source into blood and into milk and other foodstuffs and thereby enter the human body [7]. Mostly Phthalates are used as plasticizers to make polyvinyl chloride (PVC) squashy and supple [10]. Phthalates are known as endocrine disrupters. Our endocrine system is also known as hormonal system. It is one of the important systems for communicating, controlling and coordinating different body activities in mammals [12] and in all living creatures. It influences the nervous system to regulate essential body functions. These body functions include growth and development, osmoregulation and homeostasis. The endocrine system regulates reproductive processes and skeletal development [4].

The principal phthalate esters used in cosmetic products are dibutyl phthalate DBP, dimethyl phthalate DMP and diethyl phthalate DEP. They are used primarily as plasticizers in products such as nail polishes to reduce cracking by making them less brittle, hair sprays to help avoid stiffness by allowing them to form a flexible film on the hair.

Now days nail polishes are available in small bottles in liquid form along with tiny brush used for its application. The substance gets hardened within few minutes after its application and makes a layer which is water proof [3]. Phthalates are known as "plasticizers", compounds used in the production of plastics to help make them soft and pliable. They are also used in many cosmetic and personal care products as fragrances. Phthalates are so widely used in consumer products that exposure to these chemicals is universal except in the most primitive cultures. Phthalates are considered to be endocrine disrupting chemicals.

The European Union banned phthalates in soft PVC toys and childcare products in 1999 through its Commission Decision 1999/815/EC. In 2004, the EU banned phthalates in cosmetics and other beauty products. No such bans are in effect in the United States and elsewhere outside European Union. The use of personal care products (PCP) by women, mostly perfumes, lotions and fragrance products were positively associated with high urinary concentration of multiple phthalate metabolites [9]. The hazardous effects of such chemicals on life and environment emphasize the investigation of such chemicals in various products and connected to morality. The purpose of current research investigation is isolation, identification and estimation of phthalates in different nail enamels and moisturizing lotions used in Pakistan to develop the profile whether of phthalates concentration present in these cosmetics are within safe limits set by World Health Organization (WHO). According to Halden, 2010, it was assumed that worldwide annual production of plastics will exceed 300 million tons in 21st century [14].

Present investigation was done to determine presence of phthalates in locally available and branded cosmetics (nail enamels, moisturizers) available in Pakistan and to evaluate the quality of different cosmetics brands used on daily basis and to recommend most appropriate brand (nail enamels, moisturizers) for usage by comparison method.

EXPERIMENTAL SECTION

Total twenty four cosmetic samples were collected from retail stores of Rawalpindi, Pakistan. Out of twenty four, twelve samples were of nail enamels while rests were of moisturizing lotions. Most of the sample collected were locally available and were not of international brands. Samples were stored at ambient conditions for further use. Gas chromatography-Mass Spectrometric (Model No. 5050Q, Shimadzu, Japan) with DB-5 column (0.25mm*0.25 μ m) was selected for qualitative analysis.

Sample of nail enamels selected were Marlin, FHC, Xoan (reddish), Xoan (mustard), Absolute, Aristole USA, LX, Medora, Golden Rose, Paupal, Guppy and B.O nail lacquer. Samples were coded as N1, N2.....N12 respectively.

Samples of moisturizing lotions selected were Oval, Body sol, Madam, Johnsons Baby lotion, Garnier, Soft touch, Loreal Paris, Dove, Ponds, Vaseline, Navea, body shop Vit. E moisturizer, and are coded as M1, M2,.....M12.

GC-MS analysis

Sample 0.5 g of each moisturizing lotion and nail enamel separately was weighed accurately in 250 ml conical flask on electric balance. Methanol (Merck, Analytical Grade) /sample (25:5) and n-hexane (Merck, Analytical Grade) /sample (5:10) were added in each sample of moisturizing lotion and nail polish separately followed by Magnetic stirring for 20 min till homogenization. The mixture was then centrifuged at 15.000 rpm, upper clean layer

was decanted and 5 g of sodium sulphate (Merck, Analytical Grade) as added into it, to remove all moisture from mixture.

The solution was filtered by using Whatmann filter paper. The resulting solution was injected into GC-MS for qualitative analyses.

Gas chromatography–Mass Spectrometric (Model No. 5050Q, Shimadzu, Japan) with DB-5 column (0.25mm*0.25µm) was used to determine phthalates from nail enamels and moisturizing lotions. The application details are as follows: (Column length: 30 cm, Column diameter: 0.25 mm, and film thickness : 0.25µm, Injection port initial temperature: 280°C, Column Inlet Pressure : 90 kPa, Oven temperature : 75°C, electron ionization (EI) voltage : 70eV.

RESULTS AND DISCUSSION

Table 1 showed that out of 12 samples of lotions, 2 samples M2 and M6 were found to have di-butyl phthalate DBP while one M4 with di-ethyl phthalate DEP. One very important outcome of present research work was presence of terephthalic dihydrazide in most of the moisturizers. It was assumed that due to leaching of polyethylene terephthalate from plastic bottles and its reaction with hydrazine hydrate used as an ingredient in moisturizers, this toxic product was formed [15]. Most of the imported samples as well as Pakistani brands showed presence of terephthalic di hydrazide.

Nail Enamels Samples Names & codes	Phthalates		Moisturizers Sample Names & code	Phthalates		
	DBP	DEP		DBP	DEP	Terephthalic Dihydrazide
Marlin (N1)	Present	BDL*	Oval (M1)	N.D	N.D	Present
FHC (N2)	Present	N.D	Body sol (M2)	Present	N.D	Present
Xoan red (N3)	N.D*	Present	Madam (M3)	N.D	N.D	Present
Xoan mustard (N4)	N.D	Present	Johnson's (M4)	N.D	Present	N.D
Absolute(N5)	BDL	Present	Garnier (M5)	N.D	N.D	Present
Aristol (N6)	BDL	BDL	Softtouch (M6)	Present	N.D	N.D
LX (N7)	Present	N.D	Loreal (M7)	N.D	N.D	Present
Medora (N8)	Present	Present	Dove (M8)	N.D	N.D	Present
Golden Rose (N9)	Present	Present	Ponds (M9)	N.D	N.D	N.D
Poupal (N10)	Present	Present	Vaseline (M10)	N.D	N.D	Present
Guppy (N11)	BDL	BDL	Nivea (M11)	N.D	N.D	N.D
B.O lacquer(N12)	Present	Present	Body Shop (M12)	N.D	N.D	Present

Polyethylene terephthalate (PET) is the material most commonly used to make clear plastic bottles in which bottled water is sold. PET bottles are also in widespread use as containers for soda beverages, sports drinks, and condiments such as vinegar and salad dressing. PET bottles are also commonly used for the packaging of cosmetic products, such as shampoo, particularly when such products are sold in clear plastic bottles.

Seven samples of nail enamels (N1, N2, N7, N8, N9, N10, N12) were contaminated with DBP and seven (N3, N4, N5, N8, N9, N10, N12) were contaminated with DEP, (Table 1). Comparison among analyzed moisturizers showed that only Ponds (M9) and Nivea (M11) are better to recommend for use than other analyzed sample. In nail enamels every analyzed sample showed contamination of either one of phthalates DBP, DEP or both. So not even single nail enamel was favored for use.

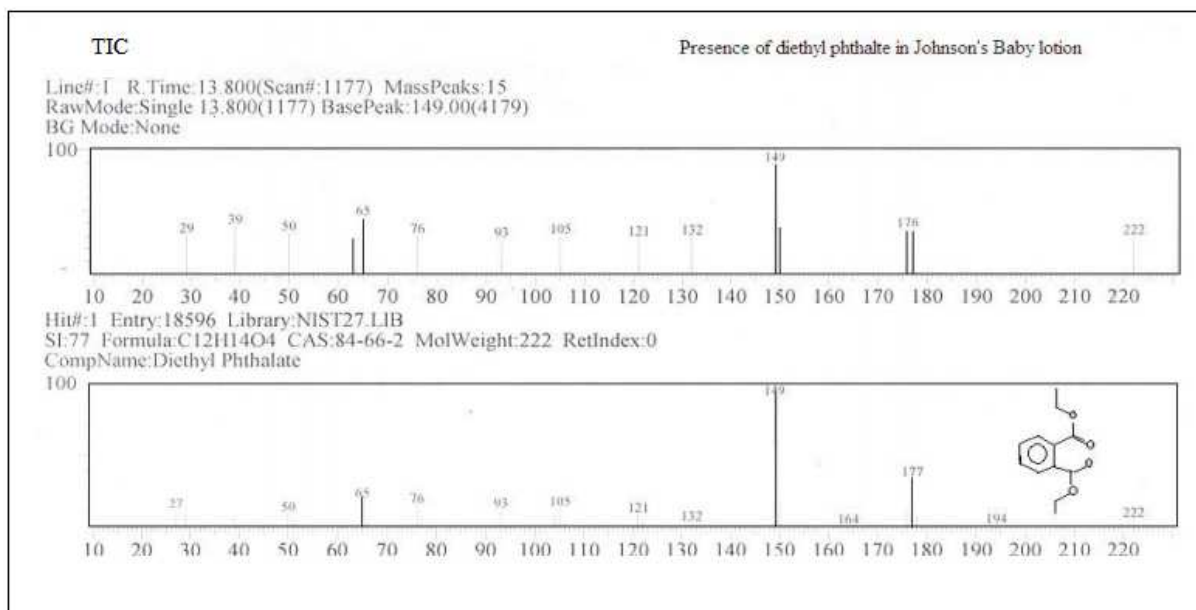
Confirmation results were found by m/z ions and its abundances using GC-MS (Table 2).

S. No.	Compounds	Confirmation ions (m/z) and the abundances
1	Dibutyl phthalate (DBP)	149(100), 65(3.89), 27(3)
2	Diethyl phthalate (DEP)	149(100), 65(66), 222 (49)
3	Terephthalic dihydrazide	43(100), 64(59), 90(57), 194(58)

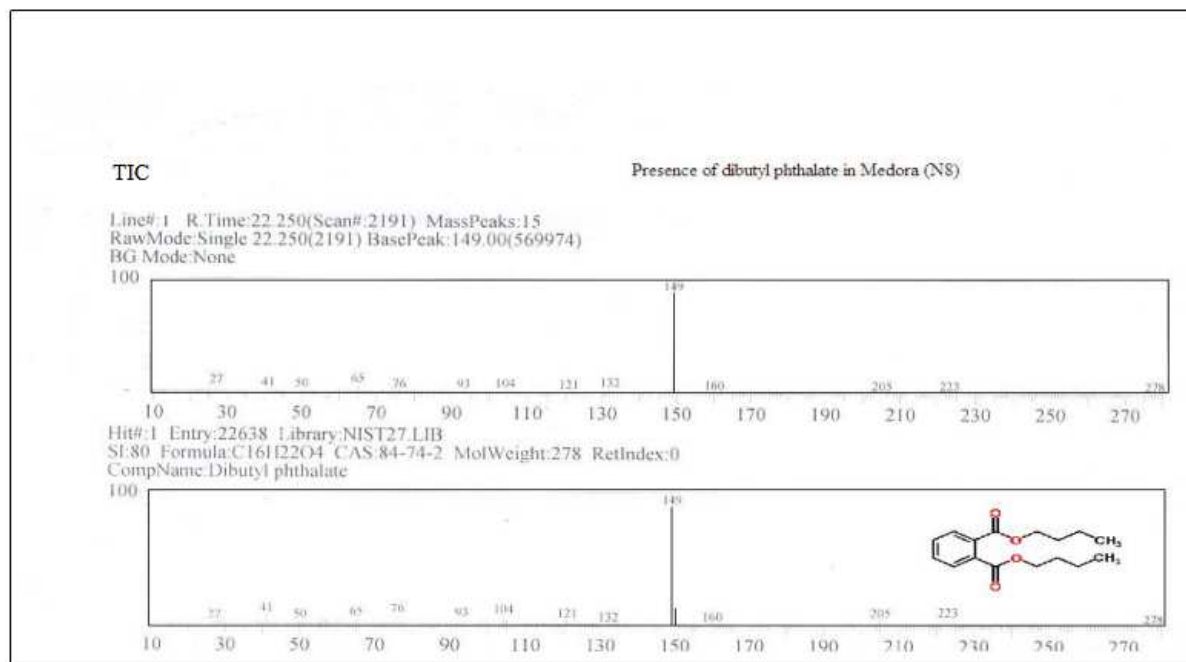
In fig (a-c) three mass spectra are attached along with TIC. As most of the people in Pakistan use Johnson's Baby lotion (M4) and Garnier (M5) as moisturizers, and both showed contamination of Phthalates and hydrazides as

shown in Fig 1 and 3. Medora (M8), commonly used nail enamel also showed contamination of di-butyl phthalate as shown in Fig 2.

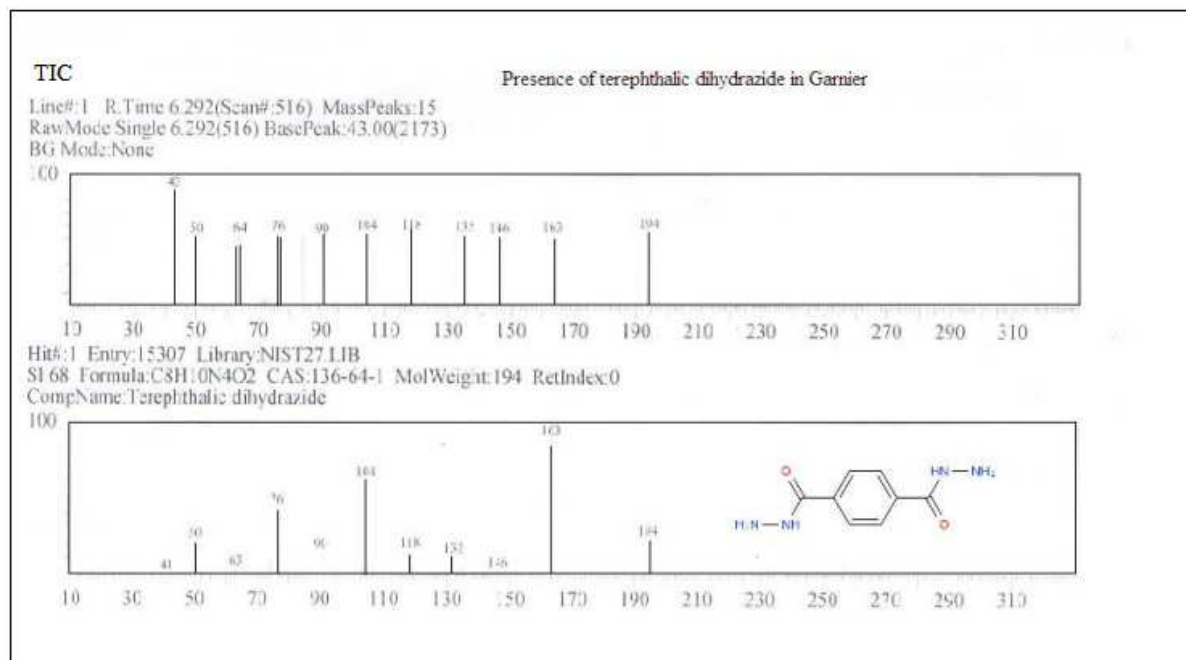
Diethyl phthalate DEP was detected in moisturizing lotions as well as in nail enamels. The constant exposure to diethyl phthalate results in paternal, immunotoxic effects as well as mechanistic data shows endocrine modulation and effect on enzymes [6]. Di-butyl phthalate has been identified in plasma and tissues of patients undergoing hemodialysis or receiving blood transfusions [5]. According to (Aylward *et al*, 2013) tolerable daily intake of 0.006 mg/kg/day was calculated for DBP and 0.01 mg/kg/day was calculated for DEP [13].



(a) TIC of Johnson's Baby Lotion



(b) TIC of Medora



(C) TIC of Garnier

Figure (a-c). TIC of Lotions and nail enamels

CONCLUSION

Analyzed samples of selected moisturizing lotions and nail enamels were not free from phthalates. Out of twelve (12) analyzed samples of nail enamels, seven samples showed contamination with DEP and seven with dibutyl phthalate DBP, while in moisturizing lotions out of twelve samples, only two (2) samples were contaminated with DBP and one with diethyl DEP. Important outcome of the present qualitative investigation was presence of terephthalic dihydrazide. According to present research work and after making comparisons among analyzed moisturizers and nail enamels, it was concluded that Nivea and ponds are better to use while not even a single nail polish was not good to use due to over contamination of phthalates. Due to their toxic effects phthalates have been banned by different health organizations but some developed as well as developing countries like Pakistan are using these as plasticizer in different cosmetics, toys, waxes etc. Special focus on Governmental and organizational levels should be required to establish the policy and its implementation regarding safety of cosmetic products in Pakistan.

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