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# CHEMICAL MIGRATION – AN INVESTIGATION OF PHTHALATES IN FOOD PACKAGING AND THEIR MIGRATION INTO FOOD

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## ABSTRACT

Migration of substances from food contact materials (FCMs) has become an important food safety issue. Key FCMs such as plastics are of interest due to their wide use and the need for migration testing of chemical residues such as phthalates. Of further interest is the investigation of nanoparticles in food, their sources, potential for migration, and possible health effects. This paper describes the current measurement approaches for migrating chemical residues such as phthalates, and proposes future investigation of the presence/absence of harmful migrating nanoparticles in food packaging.

**Keywords:** Migration, phthalates, nanoparticles, chemical residues, food packaging.

## 1. INTRODUCTION

Chemical migration from food packaging is an important issue due to the suspected carcinogenic and estrogenic properties of phthalates. Phthalates are used widely as additives in plastics and other products [1]. Bis (2-ethylhexyl) phthalate (DEHP), is by far the most commonly used phthalate, and has a wide range of applications such as use in paints, rubber products, adhesives and cosmetics [1, 2]. Health concerns regarding exposure to phthalates in food arise based on numerous studies of their endocrine disrupting properties [3] and negative effects on male foetal reproductive development.

A number of food safety and food standards agencies have imposed restrictions on the use of phthalates in food packaging. The European Food Safety Authority (EFSA) has published re-evaluations of phthalates in 2005, highlighting concern over phthalate use in PVC food contact materials [4]. In our region, the Australian Standard 2070-1999 (AS2070) outlines procedures for evaluating migration of materials for food contact use.

AS2070 was prepared between Standards Australia and Standards New Zealand Joint committee in 1999 and refers extensively to the European Commission directives (2002/72/EC, 82/711/EEC and Annex XII of EU directives) and the US Food and Drug Administration (USFDA) parts 170-199 US code of federal regulations. Currently there are 6 EU restricted phthalates of interest in food packaging and food products. These EU restricted phthalates are shown in Figure 1.

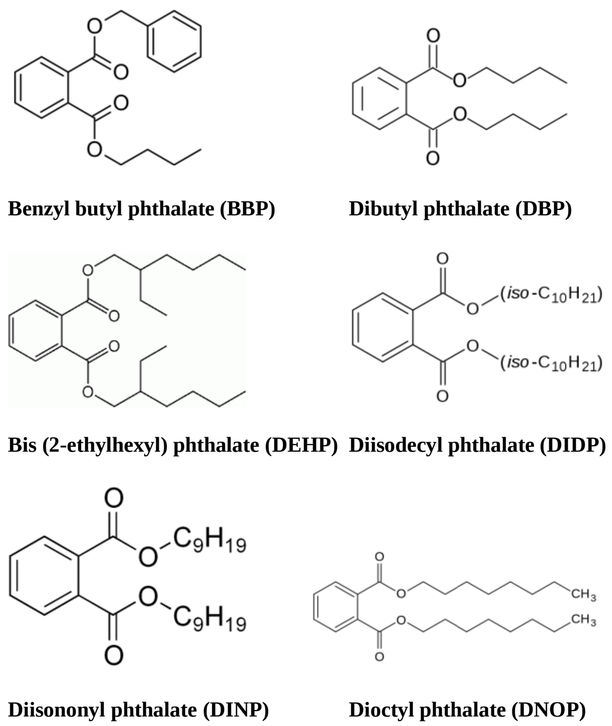


**Figure 1:** EU Restricted Phthalates

Recent adulteration outbreaks in Asia have created a further need for regular testing of food and beverages. Under the Australian Standard 2070 (AS2070), materials for testing are subjected to simulation with an appropriate simulant, followed by gravimetric determination. This research has been conducted in an effort to further identify migrating chemicals, specifically phthalates, which arise from food packaging under simulation conditions.

This paper aims to present the development and validation of a protocol suitable for testing migrated food packaging residues, and in particular phthalates using solvent and solution simulants. Food migration residue analysis was developed to help assist domestic food companies comply with local and international food safety standards. In this research study, simulation of materials was achieved using one or more of the following simulants: water, 3% acetic acid, 15% ethanol, and rectified oil. These were chosen to represent aqueous, acidic, alcoholic, and fatty foods respectively. Due to the analytical challenges of using rectified oil in chromatography systems, it was substituted with iso-octane for this research work. The rationale for using iso-octane is supported by 82/711/EEC directive.

For this developmental work, plastic and aluminium were chosen as test materials, as wraps and containers made from aluminium and plastic are widely used for wrapping and packaging foods. Four food simulants were used to determine migration values from plastic and aluminium foil as food contact materials (FCMs).

This method has been developed based on AS2070-1999 and EUCTP A0219 (85/572/EEC, 82/711/EEC, 2002/72/EC) directives for migration testing of articles for food contact use, by National Measurement Institute, Australia. The method can be used to determine if the migration levels of critical residues such as phthalates into food are within acceptable safety limits established by the Australian Standards.

## 2. EXPERIMENTAL

### 2.1 Materials

MilliQ water (Millipore™), Acetic acid (glacial), ethanol (HPLC grade), methanol (HPLC grade), Iso-octane (AR grade), dichloromethane (AR grade), acetone (AR grade), EPA 8270 internal standard (IS) mixture (40 mg/L made in methanol) and n-octyl phthalate standard (made in dichloromethane). The above chemicals were obtained from Sigma-Aldrich (Australia) and reagents from Merck.

### 2.2 Apparatus

Ruler, scissors, pre-assemble purge and trap (P+T) vial with lid 44 mL, beakers, shaking heating block with nitrogen evaporating manifold, disposal glass pipettes, gas chromatography (GC) vials, GC cap crimping toll, vortex mixer, foil, thermometer, analytical balance (5 figure balance) and an incubator were used for this work.

### 2.3 Instrumentation

Agilent™ 6890 Gas-Chromatography-Mass spectrometry detector (GC-MS) with a HP-5MS column (5%-Phenyl-methylpolysiloxane, 30 m × 0.25 mm id × 0.25 µm film thickness) purchased from Agilent Technologies™ was used for initial work. A 2µL pulsed splitless injection at 240 °C was performed in the inlet. The initial column temperature was held at 35 °C for 3.0 minutes and then increased at a rate of 50 °C/minute to 300 °C and held for a further 1.0 minute at this temperature.

### 2.4 Methods

Simulations conditions under AS2070 (1999) involved the use of 4 primary simulants to mimic acidic, fatty, aqueous and alcoholic conditions. The levels of phthalates migrating under these conditions were evaluated to assess conformance with domestic and international guidelines such as the European Economic Community (EEC 85/572; EEC 82/711; EC 2002/72) directives and guidelines.

For the initial stages of this work, phthalates were determined quantitatively by analysis and comparison with phthalates calibration standards. Plastic and aluminium were the chosen test materials in this study, as wraps and containers made from aluminium and plastic are widely used. Four food simulants were used to determine migration values from plastic and aluminium foil as food contact materials (FCMs). The simulation experimental approach is summarised in Figure 2.

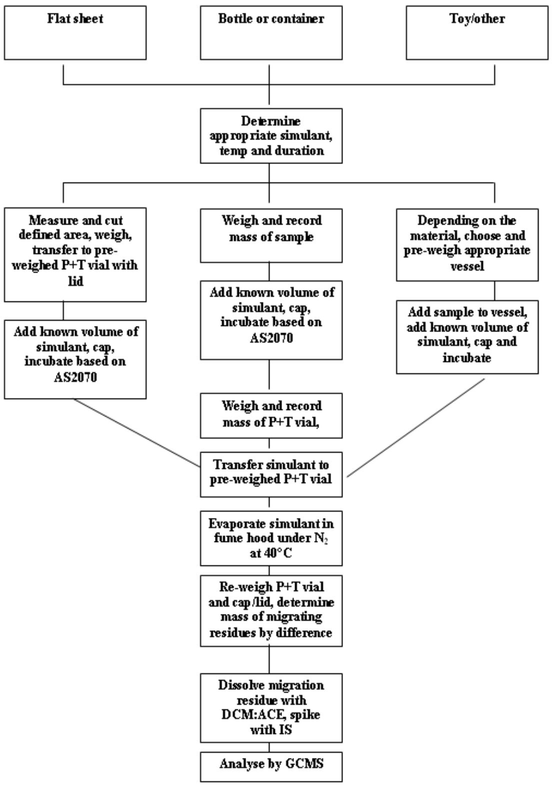


**Figure 2:** Experimental design based on FCM

All vials used for the simulation part of the migration testing were labelled (including lid), weighed and recorded. Samples of plastic and foil were added to vials and the sample mass and area recorded. The samples were spiked with oil (of known volume and mass) or a representative phthalate (n-octyl phthalate) of known concentration. A set volume of simulant was added to vials, the vials were then capped and left in the incubator at 22 °C for 10 days.

After the simulation, the plastic and foil was removed from vial. The liquid in the vial was then evaporated in a fume cupboard using a heating block with nitrogen. Vials were re-weighed and the final mass recorded. The residue from the vial spiked with n-octyl phthalate was then dissolved using dichloromethane and acetone. Internal standard was then added to the extract before transfer to a GC vial for analysis on the GC-MS instrument.

## 3. RESULTS AND DISCUSSION

Following simulation, any migrating residues were determined gravimetrically, re-dissolved in dichoromethane:acetone (DCM:ACE), and analysed by gas chromatography-mass spectrometry (GC-MS) in scan mode for semi-quantitative analysis. Blank and sample profiles were compared to determine if any significant compounds were identified by MS library spectral match. Specific phthalates were determined quantitatively by comparison with phthalates calibration standards. Table 1 shows the validation and associated measurement uncertainty of n-octyl phthalate. This method can be used to determine if the migration levels of substances such as phthalates is within the acceptable safety limits established by the Australian standards.

**Table 1: n-octyl phthalate validation**

| Calibration standard level mg/L | MU % |
|---|---|
| 3.3 | 25% |
| 4.7 | 17% |
| 6.6 | 13% |
| 8.0 | 12% |
| 8.8 | 11% |
| 9.6 | 11% |
| 9.9 | 11% |

*(MU = measurement uncertainty as percentage)*

With the exception of iso-octane, all simulants used in the method validation were simulated for 10 days at 22 °C. In the EU directive rectified oil is used to simulate fatty or oily foods; however this was not ideal for this protocol. Oil would be unsuitable as it is likely to interfere with GC-MS analysis for chemical quantitation. Alternatively, the EU directive (82/711/EEC) refers to iso-octane as a suitable substitute for fatty or oily food type simulants. However the use of the iso-octane is more aggressive than oil, therefore a shorter period of simulation was used as outlined in the EU directives to give a more accurate representation of this food type.

It was observed that the gravimetric component of the validation could be accelerated with the use of a heating block, an agitator and nitrogen to speed up the evaporation process. The samples spiked with oil resulted in two layers being formed, with the simulant being trapped beneath the oil. This presented a challenge when trying to evaporate simulant, and consequently agitation, nitrogen flow and low heat aided in evaporation; however care was taken to minimise spatter. Table 2 shows the validation of the gravimetric technique.

The highest recoveries and lower measurement uncertainty estimates based on the phthalate data was obtained from the samples simulated with iso-octane. This suggests that the long periods of simulation has a degrading effect on phthalates. The short period of simulation minimised loss of phthalates overall.

**Table 2: Gravimetric validation data**

| Simulant | Matrix | Spike level | MU (95% Cl) |
|---|---|---|---|
| Water | Plastic | 500 mg | 6.4 |
| | Plastic | 1000 mg | 3.6 |
| | Foil | 500 mg | 8.2 |
| 3% acetic acid aqueous | Plastic | 500 mg | 9.5 |
| | Plastic | 1000mg | 7.9 |
| | Foil | 1000mg | 2.6 |
| 15% ethanol aqueous | Plastic | 500 mg | 10.6 |
| | Plastic | 1000 mg | 9.6 |
| | Foil | 500 mg | 7.8 |
| | Foil | 1000 mg | 7.2 |
| Iso-octane | Plastic | 100 mg | 5 |
| | Plastic | 500 mg | 5 |
| | Plastic | 1000 mg | 5 |
| | Foil | 100 mg | 5 |
| | Foil | 500 mg | 5 |
| | Foil | 1000 mg | 5 |

*(CI = 95% confidence interval)*

## 4. FUTURE WORK

The current work is an important starting point for future studies on specific phthalates migrating from food packaging. Limited FCMs were used in this trial, and no end-product (food) testing was carried out. All data was produced based on simulations carried out under AS2070 experimental conditions. As a result, further research work is underway to carry out time-dependent experiments to evaluate rate constants and diffusion co-efficients for the 6 EU restricted phthalates in packaging.

Furthermore, a Collaborative Research Grant (CRG) has been provided by Victoria University for this collaborative research into phthalate migration from FCMs. GC-MS/MS detection of low level restricted phthalates will be used, and further studies will involve a translation of simulated results to real food systems, in particular dairy foods such as cheese. Mass transfer will be considered in these upcoming studies, allowing a comparison of laboratory simulation trials (under AS2070) in mg/L to be transposed to mg/kg values of phthalates in real food systems.

The next stages of this research work will also include an investigation of physical migration of nanomaterials from food packaging. This is an important investigation as speculation exists surrounding the possibility of nanoparticles in food, however FCMs as a potential source have not been widely studied. Currently a range of approaches are under consideration, including the preparation of a reference FCM with embedded nanoparticles for use under AS2070 simulation conditions. The implications of this proposed future study include the expansion of the current AS2070 conditions to capture both chemical and physical migration from FCMs.

## 5. CONCLUSION

A protocol was developed by NMI using the Australian Standard (AS2070) and critical components of the EU directive. The average measurement uncertainty for all the simulants was 10 % gravimetrically and 17 % for n-octyl phthalate for samples falling within the mid-calibration range (4.7 mg/L). This method is suitable for the analysis of food migration residue in plastics and foil packaging. Specific phthalates were determined quantitatively by comparison with phthalate calibration standards. This method can be used by industry to determine if the migration levels of substances such as phthalates are within the acceptable safety limits established by the Australian Standards. Further work is underway to compare laboratory simulations with real food systems by means of systematic trials on key matrices including cheese.

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