



## Detection of halogenated flame retardants in polyurethane foam by particle induced X-ray emission



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### ABSTRACT

A novel application of particle-induced X-ray emission (PIXE) has been developed to detect the presence of chlorinated and brominated flame retardant chemicals in polyurethane foams. Traditional Gas Chromatography–Mass Spectrometry (GC–MS) methods for the detection and identification of halogenated flame retardants in foams require extensive sample preparation and data acquisition time. The elemental analysis of the halogens in polyurethane foam performed by PIXE offers the opportunity to identify the presence of halogenated flame retardants in a fraction of the time and sample preparation cost. Through comparative GC–MS and PIXE analysis of 215 foam samples, excellent agreement between the two methods was obtained. These results suggest that PIXE could be an ideal rapid screening method for the presence of chlorinated and brominated flame retardants in polyurethane foams.

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### 1. Introduction

In recent years, there have been a large number of publications that highlight the potential hazards of halogenated flame retardants (FRs) in the environment [1–5] and the health concerns from human exposure [6–13]. Several of these commercial products have been voluntarily removed from the US market, including polybrominated biphenyls (PBBs, 1973) [14], pentabrominated diphenyl ethers and octabrominated diphenyl ethers (Penta-BDEs and Octa-BDEs, 2004) [15] and decabrominated diphenyl ether (Deca-BDE, 2013) [16]. Some chlorinated FRs, such as Tris (1,3-dichloro-2-propyl) phosphate (TDCPP), have been identified as suspected human carcinogens [17,18], and products containing foam treated with TDCPP must be labeled as such under California's Proposition 65 [19]. Many of the current replacement FRs entering the US market are halogenated compounds with similar chemistry, including decabromodiphenyl ethane (DBDPE), hexabromocyclododecane (HBCD), bis(2,4,6-tribromophenoxy)ethane (BTBPE), 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB), (2-ethylhexyl) tetrabromophthalate (TBPH), Tris (2-chloroethyl)

phosphate (TCEP), and Tris (1-chloro-2-propyl) phosphate (TCPP) [20–23]. All of these chemicals, both those that are new and those being phased out, belong to a class of chemicals known as organohalogens and many, with the exception of the phosphates, are defined as persistent organic pollutants [24]. Several of these are stable in the environment, bioaccumulate, and have been shown to be potentially toxic and/or carcinogenic in experiments with animals [25–30].

While halogenated FR use in polyurethane foams is prohibited in many countries, the US and UK have adopted furniture fire-safety standards that are so stringent that these laws cannot be easily met without the use of halogenated FR chemicals. For example, one of the major reasons for the wide-spread use of FR chemicals in the United States is the California Home Furnishings Bureau's flammability standard, Technical Bulletin 117 (TB 117). This 1975 legislation requires that a piece of polyurethane foam in upholstered furniture withstand an open flame for 12 s [31]. However, since so many recent scientific studies have shown these FR chemicals can be toxic and bioaccumulate in the human body, and because this story has begun to hit the mass media [32–34], the state of California has changed its legislation to adopt a smolder standard which does not require the use of FRs in products containing polyurethane foam. This revised standard, TB 117-2013, also exempts specific juvenile foam products, such as car seats,

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highchairs, changing pads, and infant mattresses, to help protect those at highest risk from these chemicals [35].

This rapidly-changing political landscape in fire-safety legislation and increasing public awareness about the potential toxicity and prevalence of these FR chemicals in our environment has led to an increasing demand to test polyurethane foam products for the presence of halogenated FR chemicals. The traditional analytical method used to identify FR chemicals in foam is Gas Chromatography–Mass Spectrometry (GC–MS). For this chemical test, a polyurethane foam sample is typically immersed in an organic solvent to extract the FR chemicals, and then the extract is reduced in volume by evaporation techniques, and injected into a GC–MS column for identification. Comparison with standard solutions can then yield quantitative evaluations and precise identification of which chemicals are present in the polyurethane foams [36–38]. The halogenated FR chemicals normally require extended analysis time in the GC–MS method because the FRs tend to pass slowly through most GC columns. The solvent extraction, evaporation, and comparison with standard solutions combined with approximately 20-min column analysis time means that the practical use of GC–MS to identify the presence of FR chemicals in foams can be tedious and expensive.

The goal of this project was to develop a rapid method to screen for the presence of chlorinated and brominated FRs using PIXE. While one can test for the presence of brominated FR chemicals with hand-held X-ray Fluorescence (XRF) instruments because the elemental bromine X-rays have sufficient energy to be measured in air, these measurements are not as reliable for chlorinated FRs due to chlorine's relatively low-energy X-rays [39]. The development of an *in vacuo* ion beam analysis method allows the concentrations of both chlorine and bromine to be quantitatively measured in a polyurethane foam matrix, and the sample preparation and analysis time can be reduced from hours per sample to minutes with a comparable reduction in cost. While PIXE analysis alone cannot identify the specific FR used, there are no typical sources of halogens within polyurethane foams that contribute to chlorine and bromine levels greater than 2–5% (by weight). This means that for rapid screening of large numbers of foam samples, such as those requested by concerned consumers of foam-filled furnishings, clothing, bedding, and automobiles, PIXE analysis could provide a viable method to test for the presence of these chemicals of concern.

There are several other potential screening methods that could identify both Br and Cl in polyurethane foams, including in-vacuum XRF systems which should be as sensitive as PIXE. However, these in-vacuum XRF systems are no longer portable and therefore the analysis method is roughly equivalent to PIXE. Newer, more advanced tabletop XRF systems are capable of measuring Cl in air, but preliminary results in a follow-up study to this work indicates that it is less reliable quantitatively than *in vacuo* studies for Cl measurements [40]. Better methods that not only perform elemental identification but also rapidly identify the FR chemicals might include techniques such as Surface Ionization with Time-of-Flight Mass Spectrometry in vacuum, or Desorption Electrospray Ionization in air. However, the primary purpose for this study is to provide a method for existing Ion Beam Analysis facilities to provide an important environmental monitoring capability while, currently, there are only limited rapid assay options.

## 2. Materials and methods

### 2.1. Materials

A TDCPP (95% pure) quantification standard was purchased from TCI America (Portland, OR). Penta-BDE, TBB, and TCPP

standards (99% pure) were purchased from AccuStandard (New Haven, CT). TCEP (97% pure) and Triphenyl phosphate (TPP, 99% pure) standards were purchased from Sigma–Aldrich (St. Louis, MO). All solvents used in this study were purchased from Sigma–Aldrich and were HPLC grade.

Polyurethane foam standards with known concentrations (8.15% and 4.76%, by mass) of TDCPP were provided by ICL Industrial Products (Beer Sheva, Israel).

### 2.2. Sample collection

Polyurethane foams samples, ranging from approximately 1 to 10 cm<sup>3</sup> in volume, were cut from couch cushions, chairs, pillows, mattress padding, and other pieces of furniture that were donated by the public. The foam samples were wrapped in aluminum foil, stored in a zippered plastic bag, labeled, and mailed to Hope College for analysis. A majority of the samples were collected by students working with the Green Science Policy Institute and the University of California, Berkeley in Berkeley, CA and the remaining samples were collected by Hope College students. A total of 215 polyurethane foam samples of known provenance were analyzed by both GC–MS and PIXE. To help confirm our findings, a subset of 24 foams were also analyzed by GC–MS at Duke University as part of a previously published study [36]. These were “samples of opportunity” that had already been completely analyzed by a reputable research group, for which there existed replicate samples in order to augment our study.

### 2.3. GC–MS methods

#### 2.3.1. Sample extractions

FR chemicals were extracted from the polyurethane foam samples by soaking a ~10 mg piece of foam in 10 mL of dichloromethane (DCM) and sonicating for 15 min. The DCM solution was then filtered into a clean vial and reduced in volume by rotary evaporation. DCM extractions were first run in the GC–MS at a 100× dilution. If no FR chemicals were detected at this concentration, further dilutions at 10×, 5×, and 1× were run until FR chemicals could be detected in the sample or the sample was run at full concentration.

#### 2.3.2. Sample analysis

Samples were analyzed using an Agilent gas chromatograph (model 6890) mass spectrometer (model 5973). Foam sample extracts were analyzed using electron impact mode (GC/EI-MS) over a scan range of 45–800 amu for the detection of TCEP, TCPP, TDCPP, TPP, TBB, and Penta-BDE. All EI spectra were compared to the NIST Mass Spectral Library. External calibration standards were used for quantification. A 0.25 mm (i.d.) × 30 m HP-5 ms capillary column coated with 5% phenyl methyl siloxane (Agilent model 19091s-433, 0.25 μm film thickness) was used for separation of the analytes. The oven temperature was set to initial temperature of 100 °C with a temperature ramp of 20 °C/min to a temperature of 200 °C, followed by a temperature ramp of 8 °C/min to a final

**Table 1**  
Retention times of FR chemicals in the GC column.

FR	Approximate retention time (min)
TCEP	7.2
TCPP	7.7
TDCPP	13.4
TPP	14.1, 15.4
Penta-BDE	17.3
TBB	17.9

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