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Affinity of charcoals for different forms of radioactive organic iodine

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ABSTRACT

During a serious nuclear reactor accident a large fraction of the radioactive iodine in the fuel can escape from the core and subsequently from the plant. While the noble gases in reactor fuel are more mobile than iodine, the iodine is often of greater concern as its chemistry and biology causes it to be more radiotoxic. Iodine has the potential to be re-concentrated *in vivo* in the thyroid. Filters containing charcoals are used both under normal operating conditions and during emergencies to retain iodine species, they are used in environmental sampling to estimate radioactive iodine and in respiratory protection systems such as air purifying filter respirators. During a nuclear accident iodine can exist in many forms. As the formation of organic iodine compounds other than methyl iodide has been observed in nuclear plants it can be reasoned that a failure of a charcoal to retain other organoiodines than methyl iodide could have adverse consequences. In this paper, the ability of different charcoals to capture various forms of radioactive organic iodine compounds has been explored. Besides elemental iodine used as reference methyl, chloromethyl, ethyl and isopropyl iodides have been studied together with iodoacetylene.

1. Introduction

During a serious nuclear reactor accident a large fraction of the radioactive iodine in the fuel can escape from the core and subsequently from the plant. During the accidents at Windscale, (Garland and Wakefield, 2007) Chernobyl (Noguchi and Murata, 1988) and Fukushima (Haba et al., 2012) large amounts of radioactive iodine were released. It is important to note that iodine chemistry during a serious nuclear accident is far from simple. (Foreman, 2015) While the noble gases in reactor fuel are more mobile than iodine, the iodine is often more important because iodine is able to form different types of reactive mobile species and it is also re-concentrated *in vivo* in the thyroid gland, which is found in all vertebrates. While medical exposures to ^{131}I do not appear to increase the incidence of secondary thyroid cancer (Dickman et al., 2003) or strongly increase the incidence of other forms of cancer (Franklyn et al., 1999) it is important to note that a link between thyroid cancer and exposure to the radioactive iodine from the Chernobyl accident (Baverstock et al., 1992) and hydrogen bomb (Takahashi et al., 2003) tests do exists. It was suggested that the difference between medical exposures and those from accidents and bomb tests might be due to either a threshold effect or that those iodine radioisotopes with shorter half-lives that emit beta particles with higher energies are more carcinogenic than ^{131}I. (Holm et al., 1988) It is assumed that the short-lived iodine isotopes released at Chernobyl only made a small contribution to thyroid doses; (Gavrilin et al., 2004) but due to their short half-lives their measurement in humans is more difficult.

During a nuclear accident iodine can exist in multiple forms, (Foreman, 2016) which have different physical and chemical properties. While iodine in the form of aerosol particles and elemental iodine can be readily captured by a mechanical filter and an activated charcoal pad (Reyerson and Cameron, 1936) some organic halogen compounds are able to pass through a charcoal pad. For example it is well known that methyl bromide can pass through a pad of activated charcoal (Clarke et al., 1945) and be released from charcoal. (Tanaka et al., 1989) While it has been claimed in one recent paper it was observed that methyl iodide absorbs onto “natural activated carbon” while methyl bromide, which was regarded as an inert gas, which would not absorb onto the charcoal. (Ramos et al., 2013) A further paper by the same authors indicates with a smaller pad of charcoal that the methyl iodide is first captured and then lost from the charcoal pad. (Ramos et al., 2011) This paper suggests that while a charcoal pad might offer some protection against shortlived radioactive iodines (such as ^{123}I) it would not offer protection against the longer lived ^{131}I unless the volume of the filter pad was very large. The nucleophilic amine 1,4-diazabicyclo[2.2.2]octane (DABCO, Fig. 1) is known to be able to convert methyl bromide into a substance which cannot easily revert to methyl bromide or leave the pores of a DABCO impregnated charcoal (Tanaka et al., 1989).

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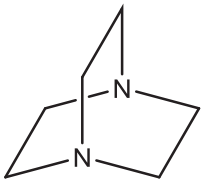


Fig. 1. The molecular structure of 1,4-diazabicyclo[2.2.2]octane (DABCO).

As prompt action is needed to protect the general public against released ^{131}I, (Drozdovitch et al., 2013) and possibly also shorter lived isotopes, after a radiological incident involving iodine, a need also exists for rapid measurement of radioactive iodine in environmental samples. Commonly iodine in air is measured by passing a large volume of air through a charcoal filter which is then later examined with gamma spectroscopy to determine the amount of radioactivity (Kitto et al., 2005). If the charcoal was to unexpectedly capture a smaller fraction of the iodine than what could be expected in such a sampling system, then an underestimate of the concentration of radioactive iodine in the environment would be made. In addition air purifying respiratory protection which uses a similar charcoal would fail to provide the expected protection to workers, while collective protection systems such as air treatment systems at nuclear plants using DABCO impregnated charcoals might also fail (Wren et al., 1999).

The filters in the respirators used by the military are normally designed to protect against a range of chemical weapons. It has been known for a long time that plain activated charcoal has too low an affinity for very volatile gases such as phosgene, cyanogen chloride and hydrogen cyanide. Therefore, to improve the performance of charcoals in such respirators, chemical additives such as amines, (Mahle et al., 2010) metals such as copper (Reucroft, 1977) and soda lime (Lamb et al., 1919) have been used to increase the charcoals ability to intercept harmful gases. If the standard respirator filters designed for chemical warfare would be suitable also for use during a radiological accident then this could greatly increase the availability of respiratory protection for use at the accident site and would enable military personal to become easily accessible for work at an accident site where assistance is needed from the military.

The formation of organic iodine compounds other than methyl iodide has been detected in nuclear plants, (Smith and West, 1967; Eggleton and Atkins, 1964; Haller and Perkins, 1967) and has been observed during experiments on model systems. (Tietze et al., 2013; Taghipour and Evans, 2000) Also within nuclear medicine radioactive iodine can be found in the form of organic compounds. For example in the effluent gases from hot cells used for the production of ^{99}Mo from neutron irradiated uranium targets (Lee et al., 1991) and in the air inside rooms where patients were treated with radioactive iodine. (Schomäcker et al., 2001) As a result the possible threat posed by other organic compounds than methyl iodide bearing radioactive iodine is relevant, rather than being a purely hypothetical threat.

Within this paper the question if a DABCO impregnated charcoal such as used for environmental sampling, respiratory protection and nuclear power plant air treatment as well as a military gas mask charcoal would be able to capture methyl iodide and other volatile organic iodine compounds relevant for radiological accident scenarios has been considered. Besides elemental iodine used as reference, the organic iodine compounds studied in this work are methyl iodide, ethyl iodide, isopropyl iodide, chloromethyl iodide and iodoacetylene (Table 1).

The more alkyl iodides, ethyl iodide and isopropyl iodide, contain halogen bearing carbons with greater steric hindrance and were chosen as they are slower to react in the S_N2 reaction compared to methyl iodide. It was previously found that chloromethyl iodide can form from dichloromethane (Taghipour and Evans, 2000) and as this solvent was commonly used as a paint solvent, e.g. in nuclear power plants, chloromethyl iodide was chosen for the study. In addition, iodoacetylene has recently become the subject of considerable interest as a reagent for the production of organic compounds (Ku et al., 2001) including pharmaceuticals bearing radioactive iodine (Avory and Trigg, 2011).

2. Material and methods

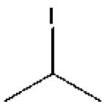
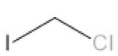
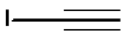
All chemicals used were of analytical grade or higher and purchased from Sigma Aldrich if not otherwise stated. The ethanol used was absolute ethanol (99.7% v/v). Radioactive iodine in form of a carrier free sodium iodide-131 solution used in nuclear medicine (GE Healthcare, provided by Sahlgrenska University Hospital) was used. The solid ^{133}Ba point source (37 kBq 15 August 2013) was supplied by Eckert & Ziegler.

2.1. Charcoal

A charcoal, from now on designated “Charcoal A”, was obtained by the disassembly of 3 M (60928) respirator cartridges. This charcoal was in the form of irregular granules a few mm in length (Fig. 2. ^1H NMR analysis (Varian Agilent 400) of a deuterated chloroform leachate from Charcoal A showed that the amine substitution of the charcoal was consistent with DABCO ($C_6H_{12}N_2$). The DABCO substitution of Charcoal A was according to elemental analysis 346 μmol g^{-1} of charcoal, while acid/base titration suggests a substitution of 381 ± 6 μmol g^{-1} of DABCO in the charcoal. The high silicon content and the K/Na ratio of 1.45 implies that the charcoal is coal-based while the low presence of metals indicates that the charcoal has not been subjected to metal substitution (Table 1).

Charcoal A was either used as obtained from the respirator cartridges, was subjected to ethanol pre-treatment to remove the amine substitution (rendering Charcoal A-1) or pre-treated with methyl iodide to chemically saturate the substituted amine (rendering Charcoal A-2). To remove the amine the charcoal was subjected to extraction with hot

Table 1
Molecular structure, boiling point and vapour pressure of A-methyl iodide, B-ethyl iodide, C-isopropyl iodide, D-chloromethyl iodide (Stolevik, 1989) and E-iodoacetylene. (Grignard and Tcheoufaki, 1929) The vapour pressure of chloromethyl iodide was calculated using the Clausius-Clapeyron equation while that of iodoacetylene was calculated using the Antoine coefficients. (Yaws and Handbook, 2015).

A	B	C	D	E
				

Molecule	Compound	Bp (°C)	Vapour pressure at 25 °C (kPa)
A	Methyl Iodidie	42.4	53.9
B	Ethyl Iodide	72	18.2
C	Isopropyl Iodide	89	9.36
D	Chloromethyl Iodide	114	4.3
E	Iodidoacetylene	32	78.9