6. ANALYTICAL METHODS

6.1 BIOLOGICAL MATERIALS

As a volatile organohalide, BDCM may be measured with good sensitivity and specificity using gas-chromatographic methods employing halide-specific or election-capture detection. Methods available for separation of BDCM from biological samples prior to analysis include headspace analysis, purge-and-trap collection, solvent extraction, and direct collection on resins.

Headspace analysis offers speed, simplicity, and good reproducibility for a particular type of sample. However, partitioning of the analyte between the headspace and the sample matrix is dependent upon the nature of the matrix and must be determined separately for different kinds of matrices (Walters 1986).

Purge-and-trap collection is well suited to biological samples that are soluble in water (Peoples et al. 1979), and is readily adapted from techniques that have been developed for the analysis of BDCM and other VOCs in water and wastewater. This method consists of bubbling inert gas through a small volume of the sample and collecting the vapor in a trap packed with sorbent. The analytes are then removed from the trap by heating it and backflushing the analytes onto a gas chromatographic column (Pankow et al. 1988). The two materials most widely used for adsorption and thermal desorption of volatile organic compounds collected by the purge-and-trap technique are Carbotrap, consisting of graphitized carbon black, and Tenax,a porous polymer of 2,6-diphenyl-p-phenylene oxide (Fabbri et al. 1987).

Solvent extraction of volatile components from biological fluids is usually performed using dimethyl ether (Zlatkis and Kim 1976). Homogenization of tissue with the extractant and lysing of cells improves extraction efficiency. When, as is often the case, multiple analytes are being determined using solvent extraction, selective extraction and loss of low-boiling compounds can cause errors. Supercritical fluid extraction using pure carbon dioxide or carbon dioxide with additives offers some exciting potential for the extraction of organic analytes such as BDCM from biological samples (Hawthorne 1988).

Analytical methods for the determination of BDCM in biological samples are given in Table 6-1.

TABLE 6-1. Analytical Methods for BDCM in Biological Samples

Sample type	Extraction/cleanup	Detection	Limit of detection	References
Adipose tissue	Purge from liquified fat at 115°C, trap on silica gel, thermal desorption	GC/HSD	<0.8 μg/L	Peoples et al. 1979
Bile acids	NR	GC/ECD	NR	Brechbuehler et al. 1977
Breath, blood, and urine	NR	GC/MS	NR	Barkley et al. 1980
Blood serum	Purge from water-serum mixture containing antifoam reagent at 115°C, trap on Tenax/silica gel, thermal desorption	GC/HSD	<0.8 μg/L	Peoples et al. 1979
Biofluids[a]	Dilute with water, sealed vial, collection of headspace vapors	GC/ECD	NR	Suitheimer et al. 1982
Grain[b]	Extract with acetone/water (5/1), dry, inject acetone solution	GC/ECD	NR	AOAC 1984

Abbreviations: GC = gas chromatography; HSD = halide selective detector; ECD = electron capture detector; NR = not reported; MS = mass spectrometry.

[a]This method for volatiles by headspace chromatography can be adapted to bromodichloromethane although the procedure does not list it specifically as an analyte.

[b]Method for carbon tetrachloride, but applicable to bromodichloromethane because of their similar properties.

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6.2 ENVIRONMENTAL SAMPLES

BDCM may be isolated from environmental samples using the same methods and principles used for biological samples, followed by gas chromatographic analysis. The most convenient procedure for most liquid and solid samples is the purge-and-trap method. A similar procedure is used for air, involving passing the air through an adsorbent canister, followed by thermal desorption.

Analytical methods for the determination of BDCM in environmental samples are given in Table 6-2.

6.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of BDCM is available. Where adequate information is not available, ATSDR, in cooperation with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine these health effects (and techniques for developing methods to determine such health effects). The following discussion highlights the availability, or absence, of exposure and toxicity information applicable to human health assessment. A statement of the relevance of identified data needs is also included. In a separate effort, ATSDR, in collaboration with NTP and EPA, will prioritize data needs across chemicals that have been profiled.

6.3.1 Data Needs

Methods for Determining Parent Compounds and Metabolites in Biological Materials. Methods are available for the determination of BDCM in biological samples, but there is a need for development of validated standard methods of analysis with well-defined limits of detection, such as those that exist for water and wastewater (EPA 1982a, EPA 1982b) and for solid wastes (EPA 1986a, EPA 1986b).

Animal studies show that BDCM is excreted via the lungs as parent compound or carbon dioxide. Small amounts of carbon monoxide have also been measured in animals after administration of BDCM (Anders et al. 1978). Other metabolites of BDCM have not been identified. Since carbon dioxide and carbon monoxide are not specific to BDCM, measurement of these metabolites is not likely to provide a good index of BDCM exposure.

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TABLE 6-2. Analytical Methods for BDCM in Environmental Media

Sample type	Extraction/cleanup	Detection	Limit of detection	References
Air[a]	Coconut shell charcoal sorption carbon disulfide desorption	GC/FID	10 µg per sample	NIOSH 1984
Air	Sorption	GC/CLMD	$3x10^{-13}$ g/sec	Yamada et al. 1982
Air and water	NR	GC/MS	NR	Barkley et al. 1980
Drinking water	Purge and trap	GC/MWED	<1 µg/L	Quimby et al. 1979
Water	Purge and trap	GC/MS	10 µg/L	EPA 1980c
Water	Purge and trap	GC/HSD	0.12 µg/L	EPA 1982a
Water	Purge and trap	GC/MS	2.2 µg/L	EPA 1982b
Water	Purge and trap	GC/HSD	0.5 µg/L	APHA 1985a
Water	Purge and trap	GC/MS	<0.27 µg/L	APHA 1985b
Water	Solvent extraction (isooctane)	GC/HSD	1 µg/L	ASTM 1988
Contaminated soil	Purge and trap	GC/HSD	1.0 µg/kg	EPA 1986a
Wastes, non-water miscible	Purge and trap	GC/HSD	125 µg/kg	EPA 1986a
Solid waste	Purge and trap	GC/MS	5 µg/kg	EPA 1986b

Abbreviations: GC = gas chromatography; FID = flame ionization detector; CLMD = chemiluminescence detection; NR = not reported; MS = mass spectrometry; MWED = microwave emission detector; HSD = halogen-specific detector.

[a]This method for halogenated hydrocarbons can be adapted to bromodichloromethane although the procedure does not list it specifically as an analyte.

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Methods for Biomarkers of Exposure. No biomarkers of exposure to BDCM are currently known. By analogy with CCl_4, it is possible that BDCM may be metabolized to reactive intermediates that form covalent adducts with cellular macromolecules. If so, immunoassays and 32 P-post labeling assays might be capable of identifying and quantifying these adducts, although levels would likely be very low. Efforts to identify such adducts and to develop appropriate measurement techniques would be valuable for determining exposure.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. BDCM can be analyzed in water, air, and waste samples with good selectivity and sensitivity. However, since BDCM may be carcinogenic in humans, very low levels in water, air or other media may be of concern, so improvements in sensitivity would be valuable.

6.3.2 On-going Studies

The development of supercritical fluid (SCF) extraction holds great promise for analysis of nonpolar organic analytes such as BDCM. Current research in this area has been summarized by Hawthorne (1988). Research is ongoing to develop a "Master Analytical Scheme" for organic compounds in water (Michael et al. 1988), which includes BDCM as an analyte. The overall goal is to detect and quantify organic compounds at 0.1 μg/L (1 ppb)in drinking water, 1 μg /L in surface waters, and 10 μg/L in effluent waters. A comprehensive review of the literature leading up to these efforts has been published (Pellizzari et al. 1985).

The introduction of capillary column chromatography has markedly improved both sensitivity and resolution of gas chromatographic analysis, but because of the very small quantities of sample required, has made sample delivery more difficult. One of the more promising approaches to sample introduction using capillary columns with purgeand-trap collection is the use of cryofocusing. Basically, this procedure consists of collecting purged analyte on a short section of the capillary column cooled to a low temperature (e.g., -l00°C), followed by heating and backflushing of the sample onto the analytical column. Several compounds closely related to BDCM have been determined in water by this method (Washall and Wampler 1988), including mefhylene chloride, chloroform, chlorobromomethane and bromoform.

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Methods are also being developed for in situ measurement of organohalide levels in water. This has been demonstrated for chloroform-contaminated well water using remote fiber fluorimetry (RFF) and fiber optic chemical sensors (FOGS) (Milanovich 1986). With this approach, fluorescence of basic pyridine in the presence of organohalide (the Fujiwara reaction) is measured from a chemical sensor immersed in the water at the end of an optical fiber. If conditions can be found under which BDCM undergoes a Fujiwara reaction, its determination might be amendable to this approach.

The Environmental Health Laboratory Sciences Division of the Center for Environmental Health and Injury Control, Centers for Disease Control, is developing methods for the analysis of BDCM and other volatile organic compounds in blood. These methods use purge and trap methodology and magnetic mass spectrometry which gives detection limits in the low parts per trillion range.