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DETERMINATION OF SOME HALOGEN ALKANES, IN SEVERAL CITIES IN ALBANIA, DEPOSED THROUGH ACTIVE INDICATORS (PARTICLES) USING THE GC/ECD TECHNIQUE.

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ABSTRACT

This study presents data for a determination method of some volatile organic pollutants (halogen alkanes) in air deposed through particles that were collected, in February 2014, in different stations in Albania. Five stations were in Tirana city, two in Durres, one in Kavaja, one in Elbasani and two in Fieri city. Chlorodifluoromethane, tetrafluoro-1,1,1,2-ethane, trichlormethane, dichloromethane, tetra chloromethane, trichloro -1,1,1-ethane, dichloro-1,2-propane, tetrachloroethylene were analyzed. The analyses of organic pollutants in air samples are limited for many laboratories because of the lack of materials for the sampling of air samples. Another limitation is that data obtained from air samples represent of-the-moment data because of vertical and horizontal air current, temperature, humidity, etc.

The quantitative analysis of halogen alkanes was performed by the gas chromatography method using an electron capture detector (ECD). The column used was a VF-1ms capillary column (30 m x 0.33 mm x 0.25 µm). The concentration of halogen alkanes in particles ranges between from 0.015 to 0.096 µg/g fresh weight sample. Dichloromethane, tetra chloromethane and, trichloro -1,1,1-ethane were detected at higher levels than other halogen alkanes obtained in the study.

Keywords: Halogen alkanes, Particle samples, Electron capture detector, Gas chromatography.

INTRODUCTION

The haloalkanes (also known as halogen alkanes or alkyl halides) are a group of chemical compounds derived from alkanes containing one or more halogens. They are a subset of the general class of halocarbons, although the distinction is not often made. Halo alkanes are widely used commercially and, consequently, are known under many chemical and commercial names. They are used as flame retardants, fire extinguishants, refrigerants, propellants, solvents, and pharmaceuticals. Subsequent to the widespread use in commerce, many halocarbons have also been shown to be serious pollutants and toxins. For example, the chlorofluorocarbons have been shown to lead to ozone depletion. Methyl bromide is a controversial fumigant. Only halo alkanes which contain chlorine, bromine, and iodine are a threat to the ozone layer, but fluorinated volatile halo alkanes in theory may have activity as greenhouse gases. Methyl iodide, a naturally occurring substance, however, does not have ozone-depleting properties and the United States Environmental Protection Agency has designated the compound a non-ozone layer depletes. Halo alkane or alkyl halides are the compounds which have the general formula ″RX″ where R is an alkyl or substituted alkyl group and X is a halogen (F, Cl, Br,I).

Halo alkanes have been known for centuries. Chloroethane was produced synthetically in the 15th century. The systematic synthesis of such compounds developed in the 19th century in step with the development of organic chemistry and the understanding of the structure of alkanes. Methods were developed for the selective formation of C-halogen bonds. Especially versatile methods included the addition of halogens to alkenes, hydro halogenation of alkenes, and the conversion of alcohols to alkyl halides. These methods are so reliable and so easily implemented that halo alkanes became cheaply available for use in industrial chemistry because the halide could be further replaced by other functional groups.

While most halo alkanes are human-produced, non-artificial-source halo alkanes do occur on Earth, mostly through enzyme-mediated synthesis by bacteria, fungi, and especially sea macro algae (seaweeds). More than 1600 halogenated organics have been identified, with bromoalkanes being the most common halo alkanes. Brominated organics in biology range from biologically produced methyl bromide to non-alkane aromatics and unsaturated (indoles, terpenes, acetogenins, and phenols). (Butler, Alison; Catter-Facklin, Jayen M. 2004) Halogenated alkanes in land plants are rarer, but do occur, as for example the fluoroacetate produced as a toxin by at least 40 species of known plants. Specific dehalogenase enzymes in bacteria which remove halogens from halo alkanes are also known.

Chlorofluorocarbons (CFC) are organic compounds that contain carbon, chlorine, and fluorine, produced as a volatile derivative of methane and ethane. Hydro chlorofluorocarbons (HCFC) are a large group of compounds, whose structure is very close to that of Chlorofluorocarbons (CFC), but including one or more hydrogen atoms. Under normal conditions, HCFC are gases or liquids which evaporate easily. They are generally fairly stable and unreactive. HCFC do not usually dissolve in water, but do dissolve in organic (carbon-containing) solvents. HCFC are chemically similar to Hydrobromofluorocarbons (HBFC), Chlorofluorocarbons (CFC) and Halons and therefore display some similar properties, though they are much less stable and persistent. HCFC are also part of a group of chemicals known as the volatile organic compounds (VOCs). CFC and H-CFC are mainly halogenated components commonly used as refrigerants, aerosol-spray propellants, solvents, and foam-blowing agents. They are well-suited for these and other applications because they are nontoxic and nonflammable, non-carcinogenic and can be readily converted from a liquid to a gas and vice versa. Chlorofluorocarbons were first created in 1928, and were first produced commercially in the 1930's by DuPont. The first Chlorofluorocarbon was CFC-12, a single carbon with two chlorines and two Fluorines attached to it. CFC has been found to pose a serious environmental threat. Studies undertaken by various scientists during the 1970s revealed that CFCs released into the atmosphere accumulate in the stratosphere, where they had a deleterious effect on

MATERIALS AND METHODS

Sampling of particle samples for halogen alkanes analysis. Precipitated particles in 1 m^2 were collected using cotton pre-extracted with methanol, in February 2014, in different stations in Albania for determination of airborne for halogen alkanes levels. Five stations were in Tirana city, two in Durres, one in Kavaja, one in Elbasan and two in Fieri city. Samples were transported to the laboratory in a refrigerator in +4^{o}C. Sediment stations were shown in Figure 1.

Treatment of samples for halogen alkanes analysis. Cottons used for sampling of particles were eluted with 50 ml methanol. A florisil column was used for cleaning macromolecular compounds by biota and particle samples. 10 ml methanol was used for elute the column. Extracts were concentrated using Kuderna-Danish to 1 ml methanol final volume. The extracts were injected in gas chromatographs with electron capture detector (ECD/GC).

Gas chromatography analysis of halogen alkanes compounds. Chlorodifluormethane, Tetrafluoro-1,1,1,2-etan, Dichloromethane, Trichloromethane, Chlorobenzenene, Trichloro-1,1,1-ethane, Tetrachloromethane, Dichloro-1,2-propane, Tetrachloroethylene, were determined by GC/ECD in all analyzed samples. Gas chromatographic analyses were realized in a HP 6890 GC Series II instrument equipped with a micro electron capture detector and split injector. The temperature of the injector was 260^{o}C and the ECD temperature was held at 280°C. The column used was a Rtx-5 capillary column (30 m x 0.25 mm x 0.25 µm). Nitrogen was used as carrier (1 mL/min) and make-up gas (25 mL/min) for halogen alkanes analyses. 1 µL extract in Methanol (extracting solvent) were injected for all samples. Three calibration points were selected with 50, 100 and 250 µg/L for Halogenated alkanes (EPA, 2002; Cohen Y, 1996; Ho-Sang Shin, 2012).

RESULT AND DISCUSSIONS

Analyze of Chlorodifluormethane, Tetrafluoro-1,1,1,2-etan, Dichloromethane, Trihclormethane, Chlorobenzenene, Trichloro-1,1,1-ethane, Tetrachloromethane, Dichloro-1,2-propane, Tetrachloroethylene, were performed using the GC/ECD technique. A Rtx-5 column was used for their separation. Figure 2 show the totals of halogenated alkanes shown in particle samples in different stations of Albania. The highest level for halogenalkanes was found to sample K (0.167µg / g), take Kavaja city. Durres Station (D2) was also contaminated with halogenated alkanes.

Distribution of halogenated alkanes in precipitated particles are shown in Figure 3. The concentration of Halogenated alkanes that were found are: dichloromethane > tetrachlormethane > trichloromethane > trichloro-1,1,1-methane. For all other halogenated compounds were not detected or their levels were lower than the detection limit of the apparatus. The highest value of concentration of halogenalkanes was found for dichloromethane (0. 096 µg/g). This connected with the origin of the polluted of these compounds in the atmosphere and their chemical stability in the environment. The main origin could be because of the use of some chlorinated materials for cleaning and for disinfectation.

CONCLUSIONS

Analyze of Chlorodifluormethane, Tetrafluoro-1,1,1,2-etan, Dichloromethane, Trihclormethane, Chlorobenzenene, Trichloro-1,1,1-ethane, Tetrachloromethane, Dichloro-1,2-propane, Tetrachloroethylene, were performed using the GC/ECD technique. A Rtx-5 column was used for their separation. The highest level for halogenalkanes was found to sample K (0.167µg / g), take Kavaja city. Durres Station (D2) was also contaminated with halogenated alkanes. The concentration of halogenated alkanes that were found are: dichloromethane > tetrachlormethane > trichloromethane > trichloro-1,1,1-methane. For all other halogenated compounds were not detected or their levels were lower than the detection limit of the apparatus. The highest value of concentration of halogenalkanes was found for dichloromethane (0. 096 µg/g). This connected with the origin of the polluted of these compounds in the atmosphere and their chemical stability in the environment. The main origin could be because of the use of some chlorinated materials for cleaning and for disinfectation.

REFERENCES

Butler, Alison; Catter-Facklin, Jayen M. (2004). "The role of vanadium bromoperoxidase in the biosynthesis of halogenated marine natural products". *Natural Product Reports* 21 (1): 180–188.doi:10.1039/b302337k. PMID 15039842.

Cohen Y (1996) Volatile Organic Compounds in the Environment: A Multimedia Perspective.

Volatile Organic Compounds in the Environment, ASTM STP 1261. Wang W, Schnoor and J,

Doi Eds. American Society for Testing and Materials, pp. 7-32.

(Ho-Sang Shin, 2012). Determination of limit of detection (LOD) and limit of quantitation (LOQ) was used to undertake quality control of the method
Global Ozone Research and Monitoring Project, Report No. 47. Geneva: Author.

NIOSH (1994). Manual of Analytical Methods 4th - US Dept of Health and Human Services Publication 94-113
Scientific Assessment of Ozone Depletion: (2002)

United States Environmental Protection Agency, (2002) EPA Test Method 8265, Volatile organic compounds in water, soil, soil gas, and air by direct sampling ion trap mass spectrometry

(DSITMS). http://www.epa.gov/osw/hazard/testmethods/pdfs/8265.pdf

Figure 1. The map of sampling for halogenalkanes analyze in Albania, February 2014

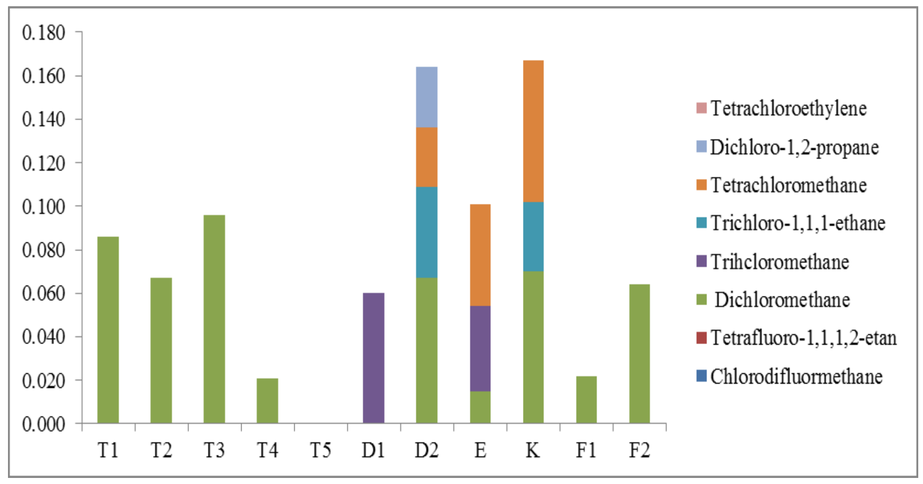

Figure 2. The totals of halogenated alkanes in particle samples in different stations of Albania.

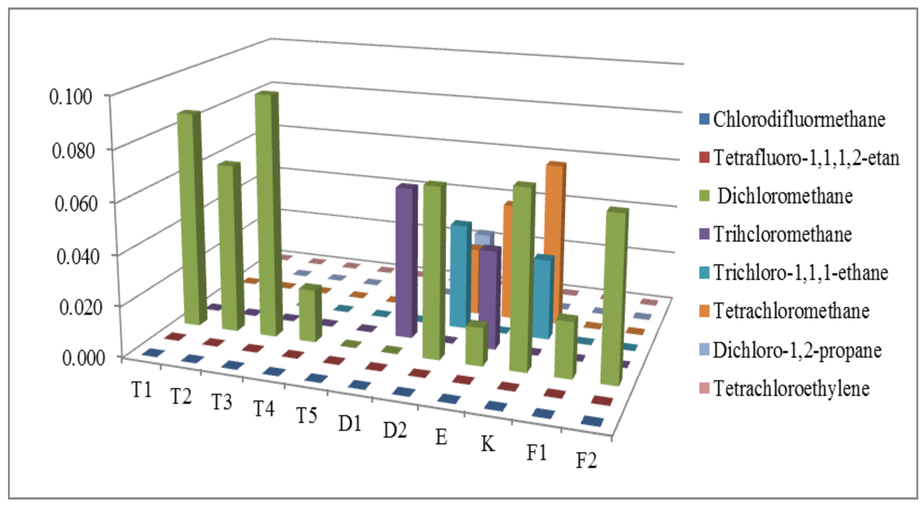

Figure 3. Distribution of halogen alkanes in particle samples in different stations of Albania