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The Pollution of 2,2′ Azobis (2 methyl propion nitrile), Chloroform and Solvent Used Acrylonitrile Polymer Synthesis in Sea Water of Yalova, İzmit Bay, Sea of Marmara

Yalova Deniz Suyu'nda 2,2′ Azobis (2 metil propion nitril), Kloroform ve Acrilonitril Polimeri Sentezinde Kullanılan Solvanların Kirliliği

Kasım C. Güven and Tuncay Gezgin

İstanbul University, Institute of Marine Science and Management, Vefa, 34470, İstanbul, Turkey

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Abstract

In this paper the identification of 2,2′ azobis (2 methyl propion nitrile), chloroform, dimethylformamide, dimethylacetamide, dimethylsulfoxide and dimethylsulphone were reported in sea waters of Yalova, İzmit Bay, Sea of Marmara. The 2,2′ azobis (2 methyl propion nitrile) was used as catalyst and the others (except chloroform) as solvent in the synthesis of polyacrylonitrile. These substances are discharged from the acrylonitrile polymer factories but the origin of chloroform can not be explained.
The identification of these subtances in sea water was made by GC/MS.These compounds are toxic for marine life hence regular measurement must be made in this region.

Keyword: 2,2′ azobis (2 methyl propion nitrile), chloroform, dimethylformamide, dimethylacetamide, dimethylsulfoxide, dimethylsulphone

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Introduction

After the earthquake occurred in 17 Aug. 1999, 6700 tons acrylonitrile spilled in environment of 15 km east of Yalova in İzmit Bay. It appears that the majority of acrilonitrile either reached with air during the release or was discharged to the Sea of Marmara. It is one of the catastrophic disasters of the world. Polyacrilonitrile fibre factory is located by the southern coast of the Sea of Marmara ~ 15 km east of Yalova. In our earlier paper the acrylonitrile and its degradation product acrylamide was detected in this area (Güven and Gezgin, 2005).

The most important industrial plants in the country are concentrated in this region and the typical pollution problem thus avails. They further cause the marine pollution in the Sea of Marmara. These plants use or synthetise various organic compounds and give bay products in the İzmit Bay.

Acrylonitrile is miscible with most organic solvents and 7.35 part dissolve in 100 part water. It gives azeotropic mixture with organic solvents (Mark *et al.*, 1964; Ulmann, 1974). It is explosive, and mixture with air is flammable. It may polymerize spontaneously in particular in case of absence of oxygen, or on exposure to visible light. Acrylonitrile is not stable and hydrolyse products are acrylamide and acrylic acid (Sax, 1974; Zhank, 1999). It is highly toxic and shows cyanide effect irritating to eyes and skin, and anticipated to be a carcinogen. The permitted concentration in the air is 15–20 ppm. Its toxic action is due to liberation of cyanide ion and therefore resembles hydrogen cyanide poisoning (Knobloch *et al.*, 1972; IARC 1979; Klaasen *et al,* 1980; Moshida *et al.*, 1988; Anon, 1990; EPA 1994).

The polymers of acrylonitrile (co- and mono) are used in the field of fibres, synthetic resins, elastomers, textiles, adhesive, surface coating, plastics, dyes, surface active agents etc.

Many compounds are used in the synthesis of polyocrilonitrile such as dimethyl formamide, dimethylacetamide, dimethylsulfone, dimethylsulfoxide as solvent and 2,2′ azobis (2 methyl propion nitrile) as catalyst. These compounds are toxic and also cause pollution for the environment.
The properties of the identified substances are:

2,2′ Azobis (2 methyl propion nitrile) [2,2’ azobis butyronitrile, azodiisobutyronitrile; 2,2’-dicyano 2,2’-azopropane] (AIBN). Its formula is:

White solid m. p.99-103^{0}C. Highly flammable, may be explosive, combination with acetone or heptane, thermally unstable, harmful by inhalation and if swallowed. It is catalyst for polyacrylonitrile preparation with AIBN (Chengxun *et al.,* 1991). The optimum polymer condition is temperature of 60 ^{0}C, time 4 hour stirring of 450 rpm

Chloroform (CHCl$_3$)

Trichloromethane is colourless volatile liquide b.p. 60-62^{0}C. Slightly soluble in water when it is exposed to air and light, decomposed to the very poisonous carbonyl chloride (phosgene) and with chlorine. It depresses respiration and produce hypotension. Cardiac output is reduced and arrhythmias may develop. It is also hepatotoxic. In the USA the FDA has banned the use of chloroform because of reported carcinogeneicity in animals (Martindale, 2005).

N, N-Dimethylacetamide (CH$_3$CO-N(CH$_3$)$_2$

It is colourless crystals, m. p. 81 °C, mousey odour, soluble in water. It is carsinogenic compound. Exposure limit is 10 ppm and caused irritation corneal, liver and kidney.

N,N-Dimethylformamide (HCON(CH$_3$)2

It is colourless, mobile liquid, bp 152,8 °C, flash point 136 °C. It is toxic for human skin. TLV in air 10 ppm (skin). Exposure limit is 10 ppm. Toxicity: Damage on cornea, liver and kidney, anorexia, abdominal pain, nausea, headache, dizziness, irritant, vomiting, loss of appetite, weakness, liver damage.

Dimethylsulfoxid (DMSO) $(CH_3)_2$ SO

It is a colourless, m.p. 18.5 ^{0}C higroscopic liquid b.p. 189 ^{0}C, of slightly bitter taste miscible with water. It freely penetrates into skin and increases its permeability. It is irritant, narcotic, consultant and cause visual disturbance. It is solvent, increases the permeability of the skin barrier layer. It is teratogen and allergen. Systematic symptoms are nausea, vomiting, chills, cramps and lethargy, irritant, narcotic, convulsion, visual disturbances, anaphylactic reaction, corneal opacity.

Dimethyl sulfone (DMS) $(CH_3)_2$-SO_2

m.p. 107-108 ^{0}C.DMS was rapidly oxidized photo chemically to sulfur dioxide, methane sulfonate and sulphate.
In this paper is reported the detection of this pollutants in sea waters near by Yalova, İzmit Bay, and Sea of Marmara.

Material and Methods

The site investigation was limited to the coastal areas of polyacrylonitrile plants.In this work the monitoring was made during Sept 15, 1999-7 Sept 2000.

The samples were extracted with 3x50 ml dichloromethane (DCM). The extracts were combined and distilled at 35 °C. The residue was taken with 10 ml hexane and applied on.
GC/MS analysis: Column HP/BP 20.30 m/0.25, 0.25mm, column temperature: 40°C 75 min, 8 °C-260 °C 10 min. Split: 50/1, Carrier gas (He), flow rate: 1.5 m/min. Injection port temperature: 250 °C.

Results

The chromatograms and spectrum of detected compounds by GC/MS analysis are shown in Figs. 1-4 and Figs. 5-8 respectively

1. 2,2′ azobis (2 methyl propion nitrile) in Fig. 3 and Fig. 7
2. Dimethylformamide in Figs. 1-3 and Figs. 5 a,b
3. Dimethylacetamide in Figs. 1-3 and Figs. 6 a,b
4. Dimethylsulfoxide in Fig. 4 and Fig. 8 a,b
5. Dimethylsulfone in Fig. 4 and Fig. 9

The results showed that the samples collected in various times contain these toxic compounds. The origin of these pollutions is from discharge of polyacrylonitrile plants situated in this region. The pollutions are the most important for seawater and caused adversely effects and damages marine organisms.

Regular measurement must be made on daily/monthly basis and also to control the sewage of these surrounding plants.

Özet

Bu çalışmada 17 Ağustos 1999 depremi sonrası Yalova'daki akrilonitril polimeri üreten fabrikanın akronitril tankında meydana gelen çatlak sonucu ortama yayılan 6700 ton akrilonitrilin çevre kirliliği araştırılması esnasında deniz suyunda yapılan akrilonitril dışında tespit edilen ve buna ait polimerin sentezinde kullanılan yardımcı maddelerden 2,2' azobis (2 metil propion nitril), dimetilformamit, dimetilasetamit, dimetilsülfoksit, dimetilsülfon ile kloroform' un deniz suyundaki yaptığı kirliliğe ait analizlerinin sonuçları verilmiştir. Bu maddelerin literatürde akrilonitril sentezinde kullanıldığına dair kayıtlar vardır. Yalnız bölgede mevcut 2 fabrikadan hangisinin bu maddeleri kullandığı saptanamamıştır. Bu devamlı denize verilen kirleticiler deniz canlıları için toksiktir. Bazıları ise kanserojendir. Bu sebepten bu bölgenin devamlı kontrol altında tutulması gerekmektedir.

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Fig 1. The chromatogram of station 1

Fig 2 The chromatogram of station 2

Fig 3 The chromatogram of station 3

Fig 4 The chromatogram of station 4

Fig 5 The spectrum of dimethyl formamide a) of the sample b) taken from HP memory

Fig 6 The spectrum of dimethyl acetamide a) of the sample b) taken from HP memory

Fig 7 The spectrum of 2,2′ azobis (2 methyl propion nitrile) a) of the sample b) taken from HP memory

Fig 8 The spectrum of dimethyl sulfoxide a) of the sample b) taken from HP memory

Fig 9 The spectrum of dimethyl sulfone a) of the sample b) taken from HP memory