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Determination of Acrylonitrile and Detection of Acrylamide in Seawater by GC/MS

Akrilonitril ve Akrilamidin Deniz Suyunda GC/MS ile Tayini

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Abstract

Acrylonitrile and its degradation product acrylamide were detected in sea water near Yalova, Sea of Marmara following spill of acrylonitrile from a tank caused by the earthquake (17 Aug. 1999). The determination and detection of acrylonitrile and acrylamide were made by GC/MS analysis. Acrylonitrile was determined as 0.157-2.88 µg/l in sea water after the accident at 27 Aug. 1999 and 0.075-0.178 µg/l at 9 Sept. 1999.

Acrylamide as a degradation product of acrylonitrile was found only in one sample collected after the accident.

This is first record of determination of acrylonitrile and detection of acrilamide in sea water at 17 Dec. 1999.

Introduction

Acrylonitrile (ACN), propenenitrile, CH_2=CHC≡N is a colourless liquid with a characteristic odour and miscible with organic solvents and soluble in water as 7.2 % (Ullmann, 1974).

It breaks down completely in water in about 1-2 weeks but more slowly in high concentration. Acrylonitrile when released to the atmosphere degrades by reaction with hydroxyl radicals occured photochemically. Photo-oxydation $t_{½}$ in air is 0.56 –8.25 days. It polymerizes readily under the influence of light.

It biodegrades quickly in soil at levels less than 100 mg/kg. Soil degradation $t_{½}$ aerobic condition is 1.25 –23 days.

It is decomposed in aerobic and anaerobic conditions in aquatic environment. The hydrolysis products of acrylonitrile are acrylamide and acrylic acid and it is metabolized by *Pseudomonas chlororaphis* to acrylamide and acrylate and by *Rhodococcus rhodochrous* to a acrylate finally to L. lactate(Zhang and Stephens, 1999).

It is used for the synthesis of dyes and for preparation of polyacrylamide polymers called acrylic fiber, the raw matrerial for textiles and copolymer resin is prepared from acrylonitrile – butadiene-styrene for nitrile rubbers and resins.

Acrylonitrile is toxic and smelled at 19 ppm conc. in water. Its toxicity symptoms occured are headache (in 16 ppm), nausee (in 16 ppm), damage to red blood cells and liver, damage to skin (blister, peel, irritation, turn red) and disorientation (in 16 ppm). It caused nervous disorder

leading to death in animals. The other symtoms are irritation of the eyes and nose, flushing of the face, increased salivation, photophobia, deepened respiration, shallow respiration, vomiting, weakness diarrhea, mildjaundise, anemia, leucocytosis, increase bile pigment (Annon, 1990; Sax, 1984). Acrylonitrile is a carcinogene compound (Klaasen *et al.*, 1980). Contact of the liquid with the skin may cause dermatitis.

The toxic action of acrylonitrile was due to the liberation of cyanide ion and resembled HCN poisoning (Mark *et al.*, 1964). The secondary action is due to its own structure, independent of the liberation of the cyanide ion. The lethal dose of acrylonitrile has not been determined. The max. limit is 2 ppm in work place air for an 8 h exposure, over a week of 40 h (OSHA, The Occupational Safety and Health Administration).

EPA recommends the acrylonitrile levels in water not to exceed 0.058 ppm. The permitted concentration in the air is about 15-20 ppm.

Acrylonitrile is used also as a fumigant for grain (IARC, 1979). It caused inflamation on pulmonery system (Knobloch *et al.*, 1972).

Survival and reproduction test on *Daphnia magma* was applied by acrylonitrile (Zong *et al.*, 1996)

Procoagulant activity in alveolar macrophage was elevated b1 ACN (Bhooma *et al.*, 1992), the growth inhibited by ACN (Mochida *et al.*, 1989).

Acrylamide is a mass of colourless crystals m.p. 84,5°C, soluble in water and organic solvents. It has an abiotic effect also toxic, causes neuropathy, erythema, numbness, tingling, touch tenderness, coldness of extremities, excessive sweating, bluish- red and peeling of palms, marked fatigue, limb- weakness. Acrylamide is used for synthesis of dyes, polymers or copolymers as plastic, adhesive paper and textiles. It is cytotoxic (Orstan, 1992).

This paper reports the methods for determination of acrylonitrile and detection of acrylamide in sea water.

Material and Methods

Sea samples were taken from 15 km to the east of Yalova in İzmit Bay, Sea of Marmara. After spill, 6700 ton acrylonitrile from a tank caused by the earthquake (17 Aug. 1999) and its degradation product were determined.

The 3L sea water sample was extracted with 6x50 ml dichlomethane (DCM), anhydrous sodium was added to the extract then filtered and distilled. The residue was taken with hexane and analysed by GC/MS (HP 6890).

GC/MS analysis conditions were:
Split: 50/1
Carrier gas (He), flow rate: 1.5 m /min.
Column HP/BP 20. 30 m/ 0.25, 0.25 mm
Column temperature: 40° C/5 min, 8° C-260° C 10 min.
Injection port temperature : 250 ° C

Calibration of GC: A calibration curve is prepared by using the peak areas of ACN in a concentration of 0.08-0.8 μg/ml.

Acrylamide was detected by using HP memory.

Results and Discussion

The standard curve of acrylonitrile is shown in Fig. 1 :

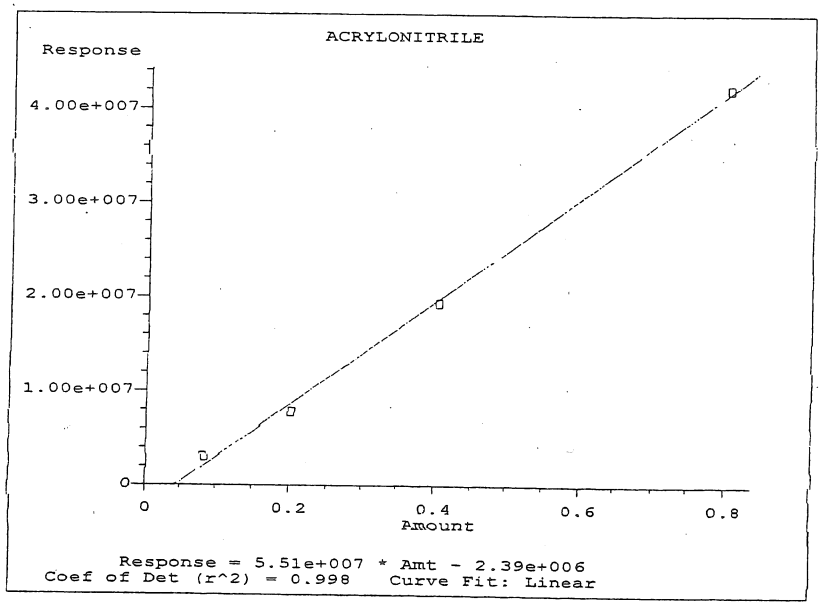

Fig.1. Standard curve of acrylonitrile

Its equation is: x= 5.51 C- 2.3q r^2 : 0.99

GC/MS chromatograms and spectra of acrylonitrile and acrylamide are shown respectively in Fig 2 and 3.

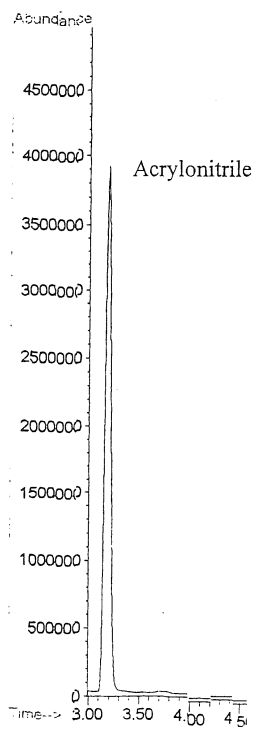

Fig.2a) GC/MS chromatogram of acrylonitrile

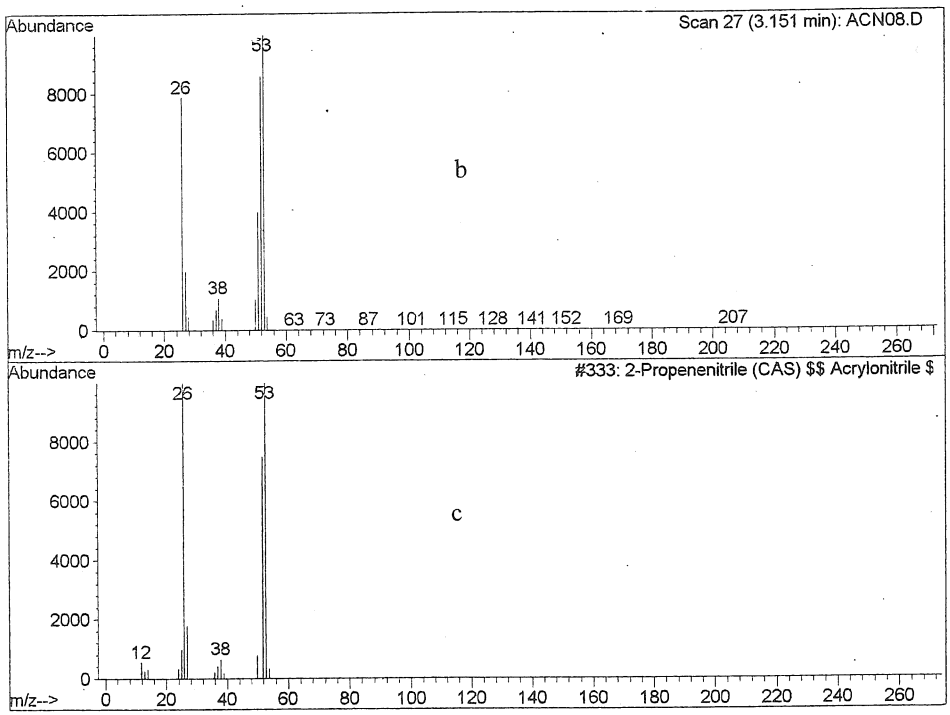

Fig. 2b)The spectrum of acrylonitrile
2c)The spectrum of acrylonitrile taken from HP memory

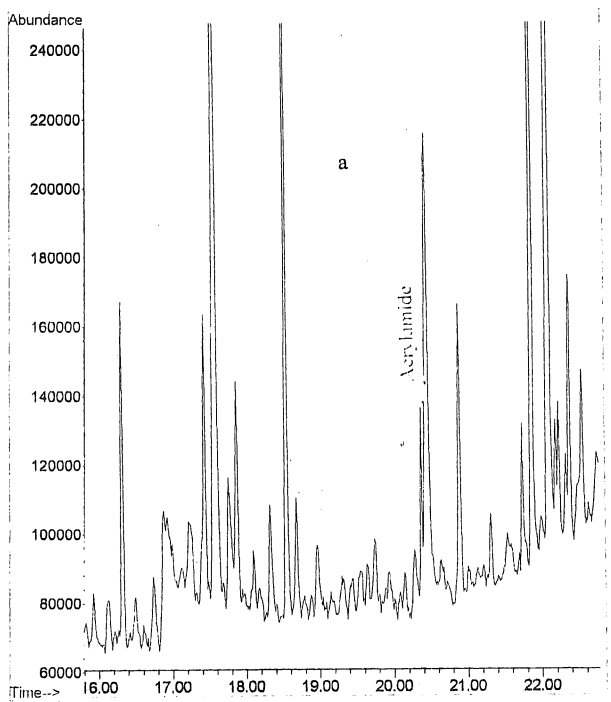

Fig.3. a) GC/MS chromatogram of acrilamide

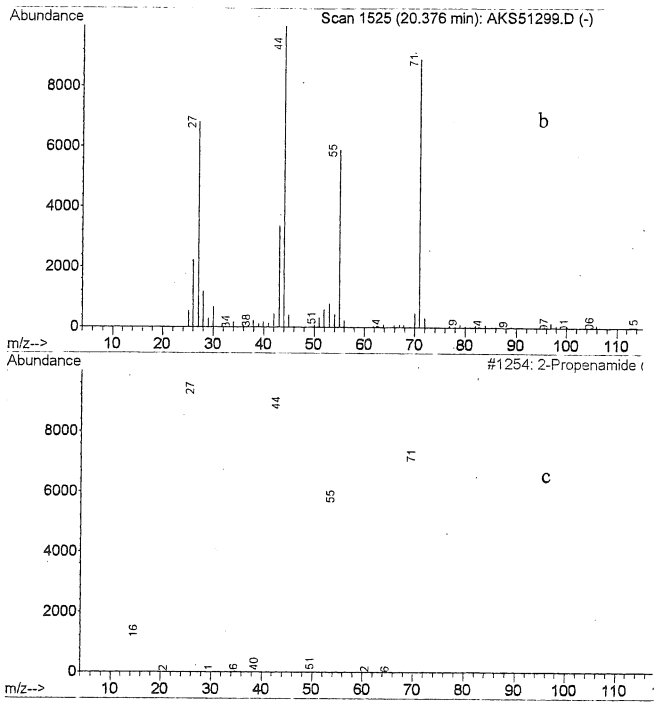

Fig. 3b) The spectrum of acrylamide
3c) The spectrum of acrylamide taken from HP memory

Acrylonitrile amounts μg/L in sea water samples are shown in Table 1:

Date / Station	27 Aug 1999	9 Sept 1999
1	0.199	0.075
2	0.157	0.163
3	2.880	0.178

Table 1. Acrylonitrile amounts at the stations 1-3

Acrylamide is detected at one station after the accident. Its chromatogram and spectrum are shown in Fig. 3 a -b and c respectively.
Nitrile group is generally hydrolysed into corresponding amide or acid. In this work only acrilamide is detected but not acrylic acid in sea water after spill of acrylonitrile in sea water.
This work is first the determination of acrylonitrile and degradation product of acrylamide detection in sea water.

There is no information in the litterature on acrylonitrile pollution and acrylamide detection in sea water. Hence this work is first record for the determination of acrylonitrile and degradation product of acrylamide detection in sea water.

Özet

Bu çalışmada 17 Ağustos 1999 depremi sonrası Yalova'da bir fabrikada deprem sonrası tankta meydana gelen kaza sonucu çevreye yayılan ve deniz suyuna karışan akrilonitril tayini ve bunun denizde dönüşüm ürünü olan akrilamid teşhisi bildirilmiştir.
GC/MS aletinde yapılan tayinde 3 No.lu istasyonunda denizde bulunan akrilonitrilin miktarı kaza sonrası 2.88 µg/L ve 12 gün sonra 8.178 µg/L dir.
Akrilonitrilin dönüşüm ürünü olan akrilamide ise yine bu bölgede 1 defa rastlanmıştır.
Bu denizde akrilonitril ve akrilamid tayinine ait litaratürde ilk çalışmadır.

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