

CASE REPORT

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Chemical Contamination of Soft Drinks in Sealed Plastic Bottles by Environmental Stress Cracking

ABSTRACT: A contamination of soft drinks in sealed bottles by organic solvents is reported: closed bottles full of soft drinks were accidentally placed on a cardboard soaked with thinner and the organic fluid subsequently fissured the bottom of the bottles and penetrated into the soft drinks without any apparent leakage of the soft drinks. Experiments were carried out to simulate the process: the penetration of different organic solvents into soft drinks through the bottom of closed bottles was tested. The penetration occurred only when the closed bottles contained carbonated soft drinks (CSD), indicating that inner pressure is a necessary condition for the fissuring of the bottles. This paper discusses environmental stress cracking of polyethylene terephthalate (PET) bottles by organic solvents and migration of chemicals to CSD. Experiments were conducted to determine the conditions in which PET can be permeable to poisoning organic products.

KEYWORDS: forensic science, environmental stress cracking, polyethylene terephthalate, food contamination, carbonated soft drink, polymer cracking, gas chromatography–mass spectrometry, solid phase microextraction

A news report about an entire family poisoned after drinking “Coca-Cola” from a sealed bottle they purchased in their local grocery caused a huge panic among consumers of the popular soft drink. In the forensic investigation, it was found that the plastic bottoms of three bottles that the family bought in the same grocery were turbid and cracked (Fig. 1).

Analyses of the soft drinks were carried out by gas chromatography–mass spectra (GCMS) and revealed that in addition to the usual known soft drink components, they contained a mixture of gasoline compounds with medium petroleum distillate (MPD) (Fig. 2).

At the beginning, our police investigation focused on an intentional poisoning of the soft drink at the production plant. The second stage of the investigation included both a deeper inspection of the production and transportation processes as well as the storage of the bottles. At this stage, we discovered in the storage room of the grocery a very particular cardboard box with peculiar marks on its bottom. The marks on the cardboard looked like the well-known petaloid shape of the bottle’s bottoms (Fig. 1). When the cardboard was sampled by headspace to GCMS, we detected the same unique picture of the organic mixture that was observed in the soft drinks (Fig. 2).

An immediate questioning of the grocery owner revealed that wall painting was carried out at the store. The grocery owner placed sealed bottles full with soft drinks to be sold on the same cardboard where paintbrushes soaked with thinners and paints were previously stored. The cardboard was already saturated with thinner when the grocery owner placed bottles on it. The thinner apparently cracked the bottom of the bottles and then penetrated through these cracks into the drinks. Simulations of the possible chain of events

prior to receiving the exhibits were performed to prove our hypothesis. Full and sealed bottles were placed on cardboard surfaces soaked with different organic solvents and the inner soft drinks were subsequently analyzed by GCMS. These simulations confirmed our findings and it became clear that the thinner made partial cracks in the bottom of the bottles, enabling the petroleum penetration without visible leakage of the soft drink.

We concluded that the cause of the contamination was the storage of the bottles on a plane soaked with thinners and paints in the grocery storage room.

Materials and Methods

Samples Preparation (Simulations)

Ten milliliters of solvent was poured to an open flask on a 0.5 cm thickness circular piece of cardboard. A full closed bottle was then placed on the soaked cardboard. The bottle bottom was visually examined at defined times. At the end of the experiment, the soft drink was sampled and analyzed by GCMS using the solid phase microextraction (SPME) method.

Sampling Methods to GCMS

Headspace—The exhibit was placed in a nylon bag then heated to 130°C for 15 min; 200 µL of air from the bag was sampled by a disposable syringe and analyzed by GCMS.

Sampling by Passive Absorbance—The liquid sample was placed in a beaker and packed in a nylon bag. A 2.5 cm glass tube (1.6 mm i.d.; 3 mm o.d.) plugged at the two ends by glass wool was filled by activated carbon and placed in the beakers for 48 h. The carbon was removed from the tube and placed in a conical vial; 25 µL of carbon disulfide (CS₂) was added and the vial was gently shaken. The CS₂ was sampled and analyzed by GCMS.

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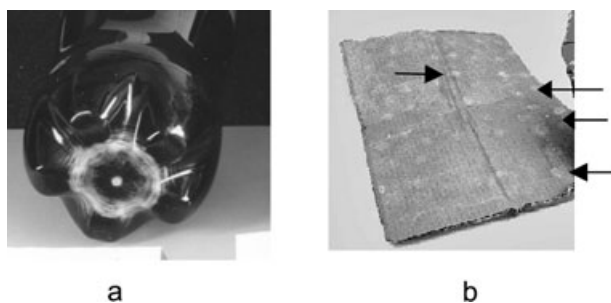


FIG. 1—Scene exhibits: (a) Cracking on the bottom of a “Coca-Cola” bottle. (b) The cardboard on which the CSD bottles were placed. Marks of the bottles are detected.

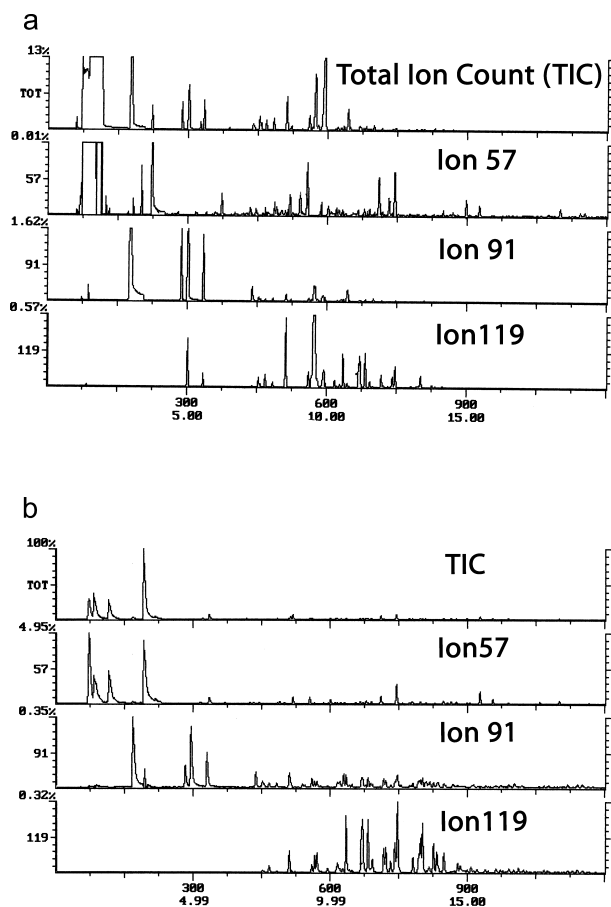


FIG. 2—Mass spectra chromatograms of scene exhibits: (a) The detected compounds in the poisoned “Coca-Cola,” sampled by adsorbance on charcoal. (b) The cardboard sampled by headspace. The same mixture of MPD with gasoline compounds can be observed in the two chromatograms with some food additives in the soft drink—57 is a typical ion present in mass spectra of alkanes, 91 and 119 are typical ions present in mass spectra of aromatic-alkylbenzenes.

Sampling by Solid Phase Microextraction—Ten milliliters of the soft drink in a flask closed by a septum was heated to 80°C for 5 min. Next, a polydimethyl-siloxane on divinylbenzene fiber was introduced by the septum to the hot headspace above the sample liquid for 10 min. The fiber was then introduced to the GCMS injector for 2 min releasing the absorbed compounds. In every case, blank sampling of the SPME fiber was performed before the test.

Equipment

Two instruments were used:

(1) A Varian Star 3400CX GC coupled with a Varian Saturn 2000 ion trap detector (Middelburg, The Netherlands). The GC column was a fused silica capillary column 30 m × 0.25 mm (i.d.) coated with 100% dimethyl polysiloxane (0.25 μm film) from SGE (Victoria, Australia). The injector temperature was 250°C. The column temperature was held at 50°C for 3 min, and then heated to 230°C at a rate of 5°C/min. The transfer line was held at 200°C. The ion trap temperature was 100°C. The scan range was 42–350 Da. The ionization times were set using automatic gain control. The carrier gas was helium. The injections were carried out in splitless mode.

(2) A Thermo Trace Ultra GC coupled with a Thermo DSQ quadrupole detector (Waltham, MA). The GC column was a fused silica capillary column 30 m × 0.25 mm (i.d.) coated with 100% dimethyl polysiloxane (0.25 μm film) from Altech-Grace (Deerfield, IL). The column temperature was held at 35°C for 2 min, and then heated to 250°C at a rate of 10°C/min. The transfer line was held at 250°C. The source temperature was 100°C. The scan range was 30–100 Da for 2 min then 25–200 for 13 min. The carrier gas was helium. The injections were carried out in split mode, split ratio: 8:1.

Exhibits Analysis

The cardboard from the grocery store and the bottom of the Coca-Cola bottles that were bought by the poisoned family were sampled by headspace and analyzed in a Saturn 2000 GCMS from Varian.

A sample from the contaminated soft drink was sampled by passive absorbance on activated carbon and analyzed in a Saturn 2000 GCMS.

Simulations

The samples were prepared as aforementioned in paragraph “Samples Preparation (Simulations).” The soft drink liquids of the simulations were sampled by SPME and analyzed by a Saturn 2000 GCMS or by a Trace Ultra-DSQ from Thermo Electron.

Materials

Gasoline and kerosene were obtained from The Israeli Refinery (Haifa, Israel); toluene AR and xylene AR were purchased from Bio Lab Ltd. (Jerusalem, Israel); cyclohexane purum was purchased from Fluka AG (Buchs, Switzerland); methylcyclohexane (#98%) was purchased from Fluka AG; Mineral Spirit was purchased from Tambour (Kiryat Sapir, Israel); CS₂ HPLC grade was purchased from Sigma-Aldrich (St. Louis, MO); the SPME fiber and holder were purchased from Supelco (Bellefonte, PA).

The soft drink bottles were from The Central Bottling Company Group, Bene-Brak, Israel (Coca-Cola, Diet Sprite, Fanta); Jafora-Tabori, Rehovot, Israel (Schweppes Soda water, RC Cola, Tapuzina Grape, Eden natural mineral water); Tempo drinks company, Natanya, Israel (Pepsi-Cola); Coca-Cola enterprise, Issy-les-Moulineaux, France (Coca-Cola); Orangina Schweppes, Levallois-Perret, France (Schweppes Indian Tonic); N.W.S. Sud, Vegeze, France (Perrier gasified natural mineral water).

Microscope

Microscopic photographs were carried out with a Wild M3Z microscope from Heerbrugg, Gais, Switzerland.

Results and Discussion

The use of polyethylene terephthalate (PET) bottles for packaging of carbonated beverages has been widespread since the 1970s. However, as far as we could ascertain, neither the literature nor the product information sheets carry any mention of the contamination of soft drinks by cracking of PET bottles.

Some early studies indicated the tendency of glassy plastic to crack when exposed to liquid environments at strain stress (1–13). The so-called environmental stress cracking (ESC) occurs when a polymer, under strain tension, is exposed to an aggressive chemical attack. ESC was studied for various polymers, for instance, reports on the cracking of polydimethylphenyl oxide (1), polystyrene, polymethylmethacrylate (2–6), polycarbonate (4,5,7), styrene-acrylonitrile copolymers (8), and polyvinyl chloride (4). Different mechanisms were proposed based on the relationship between the stress cracking and the polymer–solvent interaction: the solubility parameters (8,9), the plasticization and surface energy reducing effects (1), the liquid molecule size (2), the absorption or diffusion rate in the polymer (4,10), the polymer–solvent interaction with the molecular size, shape, and the molar volume of the liquid (11–13).

Despite the fact that ESC is well documented for a wide range of polymers, ESC for PET is less documented in the published research literature. Most of the published articles deal with the characteristics of the cracked polymer or the mechanism of the cracking (14,15). Some works examine reformulation of PET to form a blend polymer resistant to ESC (16) or the addition of modifiers to PET using the ESC properties (17). Lyu and Pae (18) designed a new petaloid pattern to the PET carbonated soft drink (CSD) bottles to prevent solvent cracking. Many reports deal with soft drink contamination by chemicals for refillable or recyclable plastic bottles when consumers store chemicals in reused plastic bottles (19,20).

Avidan et al. (21) reported about the break and leak caused by ESC in oxygenator tubes made from polycarbonate exposed to volatile anesthetics in a surgery room. That incident almost had a fatal outcome.

To the best of our knowledge, no study concerning soft drink contamination by ESC appeared in the published literature.

In the present work, simulations were performed with toluene, since it is a main product in common paint thinners, as well as with gasoline, mineral spirit, and kerosene, because of their similarity with the paint thinner that was found in the described case (a mixture of gasoline and MPD). In a second series of experiments, simulations with cyclohexane and methylcyclohexane were carried out with intent to examine the cracking phenomenon with small nonaromatic compounds.

Experiments were performed on CSD as well as on non-CSD. With non-CSD drinks, no cracking was observed even after a few days of exposure to different solvents. With CSD on the other hand, all kinds of drinks/solvents caused immediate cracking of the bottles. This confirms the literature claim that cracking appears only when the polymer is submitted to a constant stress.

In the simulations with toluene and gasoline, fissures on the bottom of the bottles could be seen with the naked eye in less than 5 min. The fissures increased with the duration of exposure (Fig. 3). The cracking effects were more significant with toluene. In one case, leaking of the soft drink was observed after 135 min of exposure to toluene. Microscopic views of the cracking of a soda bottle after 5 h of exposure to toluene are shown in Fig. 4.

A dominant smell of volatile organic compounds was felt from the CSD when we opened the bottles. Toluene and gasoline were

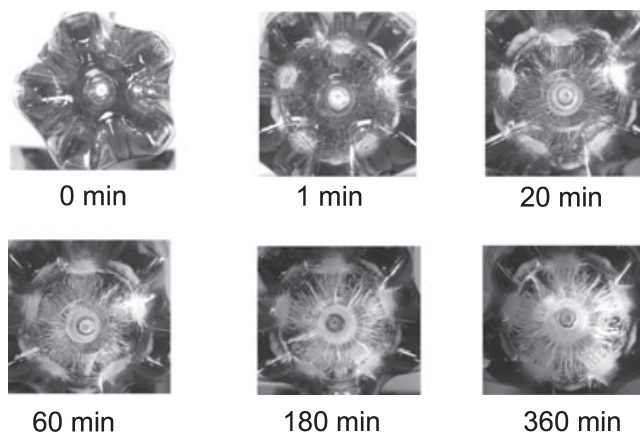


FIG. 3—The cracking progression by time of exposure of a Cola bottle to toluene.

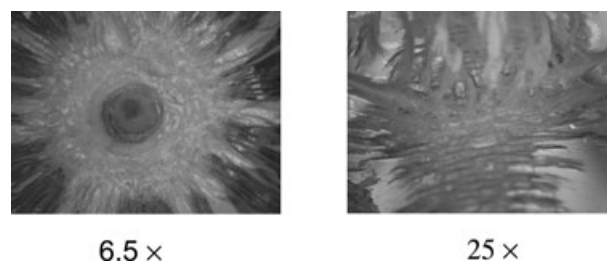


FIG. 4—Microscopic views of the bottom of a soda water bottle after 5 h of exposure to toluene (6.5 and 25 \times).

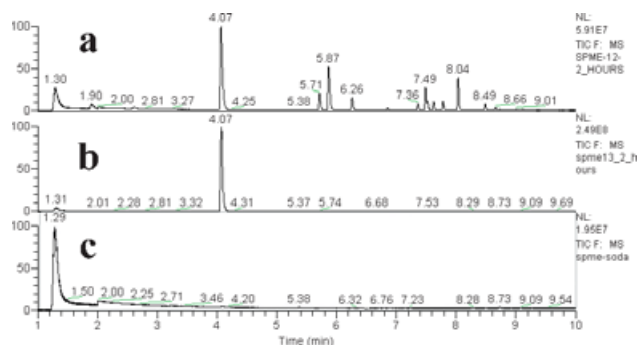


FIG. 5—Samplings of soda waters by GCMS. The closed and sealed bottles were placed on a cardboard soaked with solvent. (a) Gasoline. (b) Toluene. (c) Blank sampling of soda water. Samplings were performed by the SPME method.

clearly detected in GCMS in the soft drink after 2 h of exposure (Fig. 5).

With kerosene, fissures could be seen with the naked eye after 20 min of exposure.

Mineral spirit caused less severe cracking than gasoline and toluene: Fissures were observed after 20 min of exposure of the drink to mineral spirit but traces of these chemicals were detected in the soft drink by GCMS only after 2 h of exposure. Bottoms of sealed bottles after exposure to different chemicals for 2 h are shown in Fig. 6. Wyzgoski and Jacques (5) report that aromatic components are more severe cracking agents than aliphatic components for

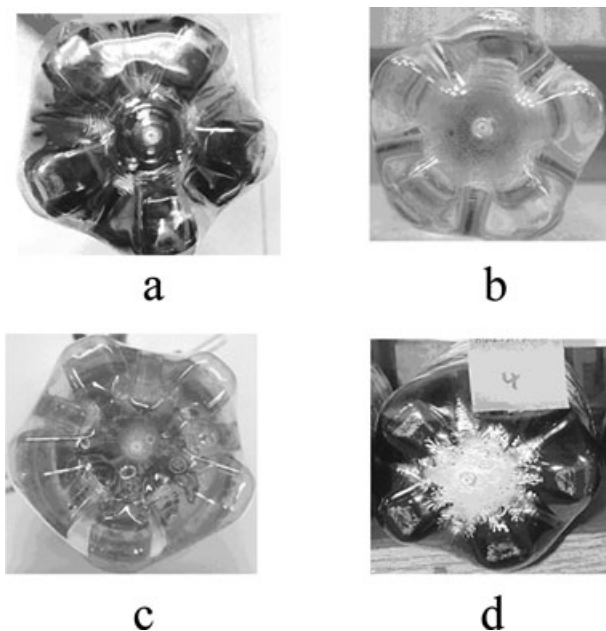


FIG. 6—Bottom of different CSD bottles after 2 h exposure to chemicals. (a) Cyclohexane. (b) Gasoline. (c) Mineral spirit. (d) Xylenes.

polycarbonate and for polymethyl methacrylate. The same correlation was observed in this study with PET.

Gasoline contains more aromatic compounds than kerosene and mineral spirits. In correlation, the cracking phenomenon was more acute upon exposure to gasoline. Toluene and methylcyclohexane have approximately the same molecular weight and the same two-dimensional structure. In the case of toluene, the cracking appeared after 10 min of exposure, with methylcyclohexane after 20 min, and with cyclohexane after 90 min. No traces of methylcyclohexane were observed in the soft drink after 2 h of exposure.

Conclusions

Environmental stress cracking is a well-known phenomenon that occurs when a polymer under strain tension is exposed to an aggressive chemical attack such as pressure from carbonation. There is a genuine concern about poisoning because of ESC, as organic products can penetrate via the polymer into the soft drink in minutes, without the awareness of the consumer.

The present case of poisoning as well as an incident reported by Avidan et al. (21) in medical equipment should shed light on other unsolved incidents.

The versatile use of polymers and the hazards related to their use led us to recommend strongly that clear warnings be affixed by the manufacturer or government agency to the relevant polymer products.

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