Fatal case at a workplace involving fluosilicate of zinc

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INTRODUCTION

Fluosilicates are salts of fluosilicic acid (eg. Al, Zn, Pb, Mg) and are used as stone consolidants (eg. Na) in production of enamel and milk glass or as insecticides (eg. Na, Mg).
Although fluorine poisonings are not as frequent as 30 years ago (1, 2), nevertheless they are still important in the field of toxicology. There have occasionally been cases of accidental or suicidal poisonings by ingestion of known or unknown amounts of fluosilicate, for the most part, sodium fluosilicate (3, 4), sometimes magnesium (1, 5), zinc or other fluosilicate.
In this paper, a case following accidental ingestion of zinc fluosilicate solution at a workplace (building) is presented.

CASE REPORT

A 38-year-old male ingested more or less 100 ml of Escofluat liquid containing zinc fluosilicate during the break in his work at the building (at about 10.00 a.m.), probably by mistake for mineral water. He was immediately transported to hospital. On admission, the patient was in poor general condition, but conscious, with limited verbal contact, reacting to pain stimuli. Gastric lavage was performed, as well as Zantac, Hydrocortisone and dopamine were administered. He was grey-tallow faced. His blood pressure was 80/50 mm Hg. In laboratory tests, the level of calcium in serum was near “zero”. At 12.50 p.m. the patient developed sudden circulatory arrest in mechanism of ventricular fibrillation. It was carried out indirect cardiac massage, and then the patient was intubated and connected to respirator. It was 15 times performed defibrillation. The man died at 13.25 p.m.

AUTOPSY FINDING

Post-mortem examination revealed only little lung oedema. Subcutaneous tissue of head and temporal muscles, as well as neck and chest muscles did not showed haemorrhages. Larynx and oesophagus were empty; in trachea and main bronchus it did not found pathological content. Oesophagus mucosa was plicate, grey coloured. Liver, spleen and myocardium were without perceptible focal lesion or change. Kidneys on cross-sections were abundantly congested. No urine was in renal pelvis and urinary bladder. Stomach contained little quantity of pale-brown liquid, mucosa did not indicated coagulation, on the whole surface occurred numerous congestions.

METHODS

1. Identification procedures

The residue of liquid which the man had drunk, found at the place of building, was examined at the Institute of Forensic Research by the use of scanning electron microscope JSM-5800, Jeol (Tokyo, Japan) connected with a X-ray spectrometer Link ISIS 300 Oxford Instruments (High Wycombe, Great Britain).
The quantitative analysis for fluoride was carried out by the spectrophotometric method with lanthane nitrate and alizarin complexone, i.e. ie. 3-amino-methyl-alizarin N,N-diacetic acid (Pye Unicam SP 6 200 Spectrophotometer, Cambridge, Great Britain) (6) and for zinc – by atomic absorption spectrometry method (Pye Unicam SP 9800, Cambridge, Great Britain). The substance was identified as 70% zinc fluosilicate.

2. Toxicological analysis

Determination of fluorine.Post-mortem peripheral blood sample as well as sections of internal organs, were examined for fluorine using the spectrophotometric method with lanthan nitrate and alizarin complexone (Pye Unicam SP 6 200 Spectrophotometer, Cambridge, Great Britain) (6) after isolation by microdiffusion. The homogenized tissues of internal organs (3 x 1 g) and samples of blood (3 x 1 ml) were placed in the microdiffusion vessels and fluorine compounds were isolated with sulphuric acid and Tergitol 4 at a temperature 60°C. The alkaline solution with absorbed fluorine was transferred into 25 ml of volume with water. The absorbance of a blue-violet coloured complex of fluoride was measured at 615 nm. The calibration curve was linear up to 15 µg F/sample. The detection limit was 0.5 µg F/sample.

Determination of zinc.Zinc determination was carried out by flame atomic absorption spectrometry method (Pye Unicam SP 9800, Great Britain) after mineralization of samples (2 x 10 g of homogenized tissue, 2 x 1 ml of blood) by concentrated sulphuric (2 ml) and nitric (10 ml) acids in Bethge apparatus. The detection limit (DL) was 0.010 µg Zn/g. The accuracy of the method was checked through the use of reference material SRM Bovine Liver 1577b (Gaithersburg, MD, USA) (certified value: 127±16 µg Zn/g, detected amounts: 118 ± 14 µg Zn/g, n = 6).
All reagents were analytical grade (concentrated acids were Suprapure quality) and were obtained from Merck (Darmstadt, Germany). A standard stock solution of zinc 1000±2 mg Zn/l was diluted daily 1:1000. Deionised water was obtained from apparatus supplied by Barnstead (Dubuque, Iowa USA).
Post-mortem blood and vitreous humour samples were also examined for ethanol by the use of gas chromatography (Perkin Elmer Autosystem with Automatic Headspace Sampler HS40, Norwalk, CT, USA). A 200 µl-blood or vitreous humour sample was used with the headspace method. Analysis was performed by the internal standard technique.

RESULTS

The fluorine and zinc concentrations found in post-mortem blood as well as in human tissues ascertained in that case of acute fatal poisonings are presented in Table 1. They exceeded many times normal levels of these elements in biological material established at the Institute of Forensic Research, Krakow (Table 1). The gastric lavage applied in this case probably

Table 1: Fluorine and zinc concentrations (µg/g wet weight) in internal organs and blood in the described case and normal levels established at the Institute of Forensic Research, Cracow, Poland

Material	Element concentration [µg/g or µg/ml]			
	$ZnSiF_6$ poisoning		Normal levels	
	Zn (AAS)	F (spectr.)	Zn (AAS)	F (spectr.)
Brain	7.54	1.39	9.16	0.03 (1.5)
Stomach	152	-	14.0	-
Stomach content	84.4	293	5.61	0.4-0.7
Small intestine	37.5	-	14.6	-
Intestine content	19.6	63.4	24.1	-
Liver	81.0	9.49	36.0	0.06(1.9)
Kidney	39.2	29.6	35.5	0.01(2.3)
Blood	23.8	6.03	7.64	<0.5

resulted in decreasing of fluorine and zinc blood levels, as well as amounts of these elements found in stomach content and tissues.
In addition, in stomach and liver large amounts of silica were detected. Ethanol was not detected in any blood or vitreous humour samples.
For comparison, some data on fluorine concentration found in biological material in fatal cases of poisonings with sodium fluosilicate are presented in Table 2.

Table 2: Fluorine concentrations (µg/g wet weight) in internal organs, blood and urine in the cases of accidental (case 1 and 2) and suicidal (case 3) poisonings with sodium fluosilicate, by various authors

Material	F concentration in Na_2SiF_6 poisonings [µg/g] or [µg/ml]		
	Case 1* (death after 1.5 h)	Case 2* (death after 7 h)	Case 3**
Stomach	1600	10	1150
Intestine	48	12	
Liver	75.6	22	
Kidney			56
Blood			130
Urine			1940[a]

* – Krylova; poisoning after ingestion of about 0.5 g Na_2SiF_6 instaed an antihelminthic drug
** – Lech
[a] – normal urine: 0.2–3.2 µg F/ml (7)

CONCLUSIONS

Acute poisonings with salts of fluosilicic acid are relatively uncommon.
A lethal dose for sodium fluosilicate is approximately 1–4 g. The main symptoms: headache, gastro-intestinal irritant, corrosion of gastric mucosa, nausea, vomiting, abdominal pain, diarrhoea, hypocalcaemia, convulsions, shock, coma and death, which may occur within 15 min (the most often within 1 to 14 hrs) due to respiratory failure or cardiac arrest. Fluorine and zinc concentrations in internal organs and blood in fatal poisoning of zinc fluosilicate exceeded many times normal levels of these elements in biological material.

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