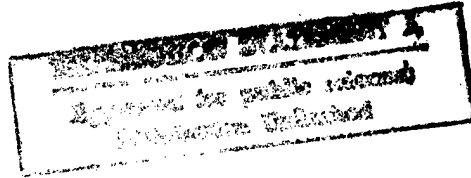


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[Article by Dan Lazarescu: "Do You Know What MOPL Is?"]

[Excerpts] MOPL is the name of a new product recently patented as an invention in Romania and in the Soviet Union. The name comes from the combining of the first two letters of the cities of Moscow and Ploiesti. This product, of petroleum origin, intended to protect metals from corrosion, is one of the results of collaboration between the Institute of Research, Technological Engineering and Design for Refineries in Ploiesti and the Union Scientific Research Institute for the Processing of Crude Oil in Moscow. Produced after 3 years of research, MOPL has proven to be an effective means of combating corrosion of metals. At present, work is being carried on in the laboratories of the two institutes to put the final touches on two other products of the MOPL series.

But this is not the only area of collaboration between the institute in Ploiesti and the institute in Moscow. Joint research is being carried on for the devising of processes for obtaining high quality fuels which would also result in a deepening of the level of processing crude oil. At the same time, the participants in the program have proposed to ensure that the new technologies consume much less energy than the methods utilized up to the present. The research takes into consideration the raw materials of each country, so that the technologies devised will be applicable both in Romania and in the USSR and so that they can also be provided to foreign partners.

The two institutes have each been assigned a schedule for each project, on the basis of which the tasks have been divided in accordance with the experience of each institute, their technical resources and the specialization of the researchers. The fact that a number of laboratory experiments, engineering projects and pilot station studies are carried out in only one of the institutes, thus avoiding duplication, leads to a substantial reduction of the research period and a noticeable reduction in expenses.

Other subjects and programs are the object of joint research by the Ploiesti institute and institutes with a similar specialization in Kiev (in the field of lubricants) and Novosibirsk (in regard to a series of catalyzers). But all these things are only a small part of the extensive Romanian-Soviet collaboration which is being carried out in the most diverse fields of activity.

CSO: 2702/14

TEXTBOOK COVERS TOXIC AGENTS, DECONTAMINATION

East Berlin LEHRBUCH DER MILITAERCHEMIE in German 15 Feb 76 No 2, pp 3-7, 9-11, 13, 15-29, 31-46, 49-53, 55-57, 59, 71, 95-96, 195, 249, 287, 295-298, 401, 437, 443, 481-482, 563; 2nd revised edition with 83 tables and 51 illustrations; Military Publishing House of the German Democratic Republic

[Volume 2. Sabotage and Plant Poisons, Detoxification and Detoxification Agents, Analysis of Chemical Warfare Agents and Poisons, team of authors: Chemical Engineer Maj Siegfried Franke (chapters 14-19, new version of chapters 20-23), Chemical Engineer Peter Franz (chapters 24, 33), Professor Dr Gerhard Gruemmer (collaborated on chapters 17-19), Chemical Engineer Lt Col Werner Warnke (chapters 20-23); signed to press on 15 February 1976; 2nd revised edition, 4,000-7,000; Military Publishing House of the German Democratic Republic (VEB), Berlin, 1977]

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[pp 9-11]

One basic concept of the imperialist general staffs is to neutralize the enemy's rear areas in wartime. Here, considerations are not so much aimed at the employment of conventional but rather at the employment of chemical and biological (bacteriological) mass annihilation methods as well as nuclear weapons. The possible use of so-called sabotage poisons takes up considerable space in these considerations.

The idea of poisoning food, water supply plants, consumer items, agricultural crops, and livestock, in order directly or indirectly to harm the enemy, is very old, with a few exceptions, the formerly known poisons permit hardly any large-scale mass annihilation.

Many of the known warfare agents used in combat are suitable as sabotage poisons. This applies particularly to phosphororganyle, Yperite, psychotoxic compounds, and toxic warfare agents. In addition, we know a number of highly poisonous substances which can partly be illustrated synthetically and which partly can be isolated from natural products and are suitable for sabotage. These are mostly compounds which cannot be used as combat warfare agents or which cannot be used because of their physical-chemical properties.

According to the "Dictionary of United Army Terms" [as published] (U.S.A., 1953), sabotage is the action of "agents of sympathizers with the intention of interrupting the war efforts of a nation or otherwise to prevent or to disturb or inhibit the defense of a nation."

Rothschild, a former corps commander in charge of research and development for the U.S. Army Chemical Corps, in 1964 estimated that sabotage is a mighty weapon already in peacetime which, used over a period of time, can lead to the destruction of the people's confidence in its country and its government and which can also be used immediately prior to or upon the outbreak of a war. He credited toxic substances with great possibilities as sabotage weapons and broadened their area of use in support of semistrategic and strategic objectives.

During both world wars, imperialist countries made great efforts to discover substances suitable for sabotage. They did not confine themselves only to poisonous substances but they also looked into bacteriological agents. After World War II, preparations became known for a sabotage war using poisons as

intended by some countries (Germany, Japan, Great Britain, the United States).

If the substances are suitably selected, sabotage poisons can be used already in small quantities by agents, by groups of subversives, by rangers, etc.; they have a great effect and, depending upon their objective, they can cause damage to man, animals, and agricultural crops.

As a result of studies on natural poisons and their analogs which in recent years have been pursued very intensively as well as investigations on their possible synthetic illustration or industrial production, the danger of the use of such substances for military purposes has increased and this means that sabotage poisons must be included in measures to provide protection against mass annihilation agents.

The substances described represent a selection (the sequence of poisons taken up is not based on any system) because the number of compounds to be considered as sabotage poisons is too great. Compounds already covered as chemical warfare agents will not be considered here with the exception of examples.

In general, the following criteria have been established for sabotage poisons to inflict damage on man:

High degree of toxicity both regarding their lethal and also their incapacitating effect;

Adequate resorption capacity through the mucosae of the digestive tract to poison water, as well as essential and nonessential foods;

Good resorption capacity through intact skin surface to poison materials, objects, and clothing;

Colorless, tasteless, and odorless;

Physical and chemical stability, especially depending upon the utilization purpose, hydrolysis and heat resistance;

Solubility in fat and water;

Delayed action in order to poison the largest possible area by the time the first phenomena of poisoning appear and to delay the determination of the source of contamination;

If possible, chemical contamination should not cause any specific pathological changes in the organism which would make it possible to recognize the particular agent;

Unusual toxic effects for which there are no or only inadequate antidotes;

Impossibility of indication in organism and in source of contamination.

These of course are idea requirements which only very few **substances** meet. The employment objective and the source selected for contamination will be decisive although the available substances last but not least will also be decisive.

Examples involving major cases of food poisoning show the extent which the application of sabotage poisons can assume.

In 1959, olive oil, mixed with aircraft engine oil, was sold in Morocco. More than 10,000 persons were poisoned suddenly.

In 1960, almost 100,000 persons became sick within 10 days in Holland after consuming a margarine mixed with a health-damaging emulsifier.

Here we might also recall the catastrophic effects of so-called gangrene from ergotism or convulsion infection which is now a part of the historical record and which sprang from the use of flour which from time to time consisted of one-third ergot. In the year 994 in France, mass poisoning caused 40,000 deaths. According to history, there were about 300 mass poisoning incidents until the 19th century.

[p 13]

14. Natural Poisons

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14. Natural Poisons

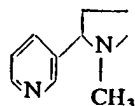
Natural poisons from plants and animals have been known for a long time and were used both for military purposes (arrow poisons, etc.) and in medicine even before their isolation became possible and before their composition became

known. Many natural toxins have not been completely identified and defined to this very day in terms of their composition and constitution. Natural toxins are formed in many different ways, in plants, animals, and microorganisms. The biochemical processes which take place here have not yet been clarified in all cases. Many are more poisonous or just as poisonous as synthetic poisons. In the substances which are of interest here we are dealing with alkaloids or toxins, some of which can be illustrated synthetically or analogs can be made on the basis of their model. All substances already covered under the heading of toxic warfare agents must at the same time be considered as sabotage poisons.

14.1. Poisons of Vegetable Origin

14.1.1. Alkaloids

14.1.1.1. Nicotine



(14.1)

3-N-Methyl-pyrrolidyl-(2'-)pyridin

Nicotine is built up in the roots of the tobacco plant (*Nicotiana tabacum*) and is transported from there into the plant. The plant's nicotine content varies according to the type between 0.5 percent and 8 percent. Nicotine-rich plants, which are cultivated especially to obtain nicotine and to make tobacco lyes [liquors], can contain up to 15 percent.

Nicotine can be illustrated synthetically. The requirement is generally met by the natural product. It is a colorless oil which turns brown in the air. In the purest state it becomes odorless, Kp [coagulation point? dissociation point?] 246° C (partial decomposition); F [melting point] below -30° C.

Nicotine is soluble in water and organic solvents. It is water-vapor-volatile. It forms salt-like compounds with acids. Nicotinic acid (Pyridin-3-carbonic acid) results from oxidation.

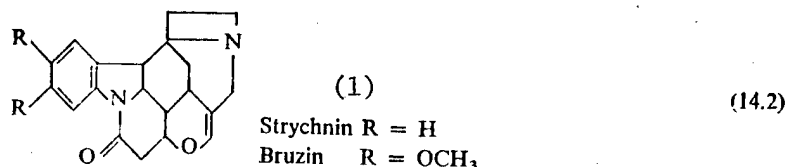
Nicotine quickly penetrates into the skin and mucosae. It is particularly dangerous when it gets into open wounds.

The lethal dose for rabbits (i. v.) is 6 mg/kg. Some animals, such as goats and does, are immune to nicotine. The lethal quantity for man is estimated at 50-100 mg. But 3-5 mg already will cause severe symptoms of poisoning such as breathing difficulty, severe cramps, and fainting spells lasting 3 days or more. Nicotine acts upon the CNS. Because it is soluble in water and fat, it can be used for poisoning essential and nonessential foods.

14.1.1.2. Strychnose Alkaloids

The Indian nux vomica (*Strychnos nux vomica*) and numerous other types of strychnos, in addition to other alkaloids, contain strychnine and bruzin (2-3 percent). Both alkaloids are of the indole type and are related to each other.

Bruzin represents the dimethoxy derivative of strychnine.



Key: 1--Strychnine.

Both alkaloids can be illustrated synthetically. Strychnine and bruzin are colorless, bitter-tasting crystals; the melting point: 268° C, bruzin 178° C. They are dissolved to a limited extent in water and in organic solvents. Strychnine nitrate and sulfate--both of which are colorless crystals--are dissolved better. Their solutions react neutral. They taste bitter.

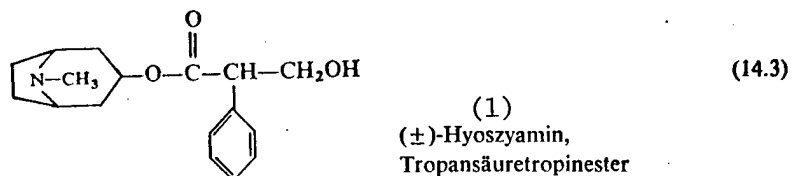
With alkalis, strychnine forms tryptamin under aggravated conditions. Strychnine takes on a blue-violet color due to the action of concentrated sulfuric acid and chromic acid.

Both alkaloids resemble tetanus toxin in terms of their toxic effect. Strychnine increases the sensory perceptions and the excitability of reflexes. Higher doses are followed by anxiety, trembling, speech disorders, painful stiffness of muscles, stiffness of the neck (the head is pulled to the rear), and distortions of facial features. The first "spasm" appears instantaneously as a result of external stimuli (noises, light). Exhaustion and the central paralysis of the respiratory center cause the lethal outcome of this poisoning. The cramps which come before death increase constantly. They are extremely painful and agonizing.

Doses starting at 15 mg can be lethal in adults and those starting at 5 mg can be lethal for children. Doses of 100-300 mg have an absolutely lethal effect. In doses of around 1 g, death occurs within 30 minutes due to paralysis of the respiratory center.

Because of its powerful toxicity, strychnine was a poison that was frequently used for purposes of assassination over a long period of time; it was used above all in pastry, sweet wine, wafers, and similar items. Bruzin is about between eight and forty times less poisonous than strychnine. Both of them are suitable for poisoning sweetened essential and nonessential foods.

14.1.1.3. Atropine



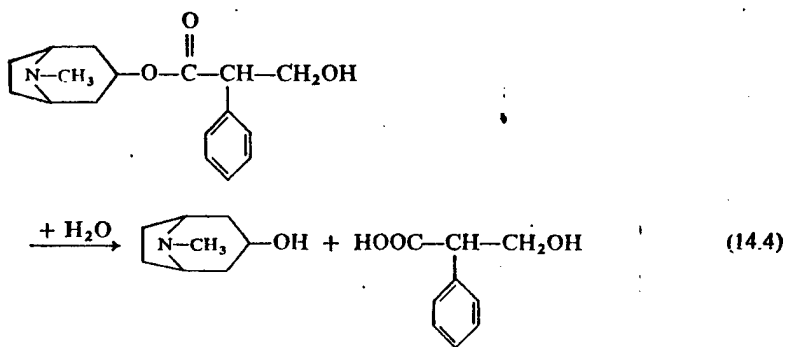
Key: 1--Tropanic [tropeinic] acid tropine ester.

Atropine occurs in belladonna (*Atropa belladonna*); optically active (-) hyoszyamin is furthermore found in other solanaceae (henbane, scopolia type, mandrake). Atropine and (-) hyoszyamin are isomeric and differ from each other only in that the latter, as acid component, contains optically active tropanic [tropeinic] acid. The main affect of atropine is credited to the content of (-) hyoszyamine. Atropine can be illustrated synthetically.

Atropine forms colorless, needle-shaped crystals which are dissolved in water to a limited degree. It has a repugnantly bitter, tart taste. It is soluble in organic solvents (alcohol, ether, chloroform) and in fatty oils.

While crystalline atropine sulfate is dissolved rather well in water and alcohol but not in ether and chloroform; melting point: Atropine, 115° C, (-) hyoszyamin 168.5° C, atropine sulfate 183° C.

Aqueous atropine solutions react slightly alkaline. Upon heating, hydrolysis takes place into tropine and tropanic [tropeinic] acid. Atropine is oxidizable.



In small doses, atropine or hyoszyamin excite the CNS while larger doses paralyze it. Taken orally, it is quickly resorbed in the gastrointestinal tract.

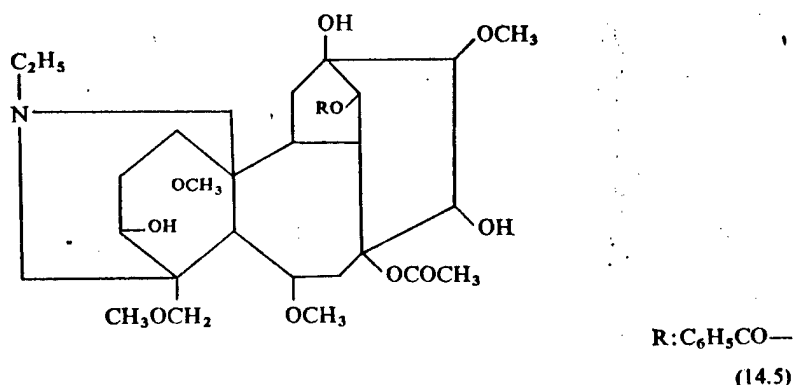
The subcutaneous dose for man is around 15 mg/kg of body weight. Depending on the doses administered, the following symptoms appear according to Hausschild:

0.5 mg: Dryness of skin, slowdown in heart rate;
 0.5-1 mg: Dryness in mouth, thirst;
 1-2 mg: Widening of pupils, heart acceleration;
 3-5 mg: Restlessness, muscular weakness, trouble swallowing, headaches;
 7 mg: Maximum widening of pupils, lack of muscle coordination;
 More than 10 mg: Apathy hallucinations, states of delirium, unconsciousness;
 More than 100 mg: Respiratory paralysis.

Hot, scarlet skin, temperature rise, trembling of limbs and constant movement of limbs are characteristic of atropine poisoning. The effect on the CNS is expressed through a compulsion to talk, dancing, fits of laughing, raving, and mania. Atropine acts as psychotomimetic.

Atropine is used therapeutically as antidote to suppress the effect of muscarine and nicotine due to the accumulation of acetylcholine following contamination with phosphororganic compounds and is a component of medical aid pouches.

14.1.1.4. Aconitine



Aconitine occurs in various types of aconitum, for example, in genuine blue monkshood. It is one of the most powerful plant toxins.

The colorless, board-shaped, odorless crystals (F 197-198° C) are almost insoluble in water but they are soluble in organic solvents (alcohol, ether). The aqueous solution reacts alkaline. The salts are better soluble in water.

Aconitine is decomposed in water, by means of alkalis and acids, especially in case of heating. Acetyl and benzoyl groups are separated due to alkali liquors and we get aconine.

Initially, aconitine excites the respiration which however later on under certain circumstances can slow down all the way to respiratory stop. After the poison's resorption, the entire body is seized with a crawling sensation (as if ants were running); this is followed by chills and perspiration, a feeling of cold, paralysis of skeletal musculature (tongue, face), vomiting, a sensation of retching, and an increase in motor unrest. The poisoning victim

will rear up and then throw himself down again. Consciousness is preserved until death (heart stoppage, respiratory paralysis).

Death can take place within an hour.

The oral dose lethal for man is reported to be about 2-5 mg. For horses, we have an LD₅₀ of 0.004 mg/kg, for rats we have 0.11 mg/kg in case of i.v. administration.

The German fascist SS during World War II conducted cruel experiments with aconitine nitrate on inmates in the Buchenwald Concentration Camp. Marksmen would hit them in the thigh with projectiles that had been poisoned with this substance.

The first symptoms appeared after 20-25 minutes (motor unrest, slight flow of mucous). The flow of saliva increased after 40 minutes and became so heavy that the poison victims were no longer able to swallow it (retching, vomiting). Motor unrest increased tremendously (individuals rearing up, throwing themselves down, rolling the eyes). Unrest abated later (widening of pupils). These agonizingly murdered people died 121-129 minutes after they were hit by the projectile.

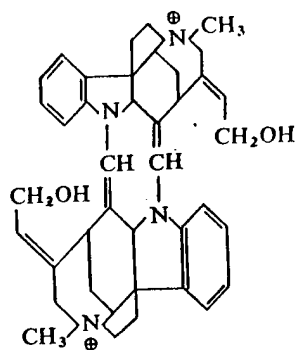
This example shows that such alkaloids and other poisonous substances can be used by means of poisoned projectiles. Aconitin and its related alkaloids (aconitines) can be used as sabotage poisons especially to contaminate essential and nonessential foods which do not have to be heated.

14.1.1.5. Curarine

Curarine has been known as an arrow poison since the 16th century. It is a brown, water-soluble, bitter mass which is obtained from the bark of liana [climbing] plant (*Strychnos toxifera*, *St. Castelniaei*) by means of aqueous extraction. We distinguish between tubocurarine and the more effect gourd curare. It contains the most poisonous plant alkaloids known so far.

The curare alkaloids are derivatives of indole. Gourd curare contains two alkaloid groups, one with about $C_{20}N_2$ and the other one with about $C_{40}N_{2-4}$, whereby the latter reveals the greater toxicity. Among them we have C-calebassin, C-curarine, and the toxiferines (C-toxiferine-I, C-Dihydrotoxiferine). The toxiferines or C-alkaloid E are the most poisonous curarine constituents.

C-toxiferine-I is believed to have the following makeup (Wieland, Pistor):



(14.6)

It is between five and ten times more poisonous than aconitine. Unpurified gourd curarine is about ten times less poisonous. The lethal dose of tubocurarine chloride for man is between 0.25 and 0.4 mg/kg of body weight. It is between 10 and a 100 times less poisonous than toxiferine or C-alkaloid E.

Curarine is not reduced in the gastrointestinal tract and is resorbed only slowly. It remains unaltered in the urine. Oral doses of curarine therefore are much less effective than in other types of application. If it is not contained in excessively large quantities, meat or other essential foods poisoned with curare can be consumed. Curare, which has gotten into the organism via other routes or through flesh wounds, will lead to the depolarization of the receptors of the motor end plates and to paralysis. It is reversible. Curarine paralysis starts with the face musculature (initially, the outer eye muscles, followed by the throat and neck muscles). Next, the musculature in the abdomen, the extremities, and finally in the respiratory center are paralyzed. Subjectively, contamination results in double vision, trouble swallowing, lowering of the head, respiratory difficulties, and others. In case of i.v. injections, the effect takes place after 2-3 minutes.

Curarine and its alkaloids are most effective when they get directly into the blood circulation through small wounds.

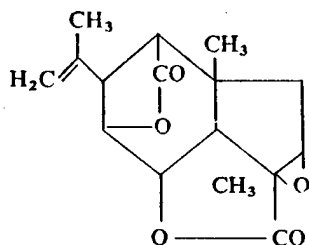
The curare alkaloids are not suitable for poisoning essential and nonessential foods. They can be used through prepared projectiles or the like.

Other highly toxic alkaloids for example are erythrophlein, homatropine, Kolchizin, Koniin, physostigmin, Veratrin, and anisatin.

Anisatin, $C_{15}H_{20}O_8$, is the active constituent of the seed of *Illicium anisatum*. The LD_{50} (i.p.) in mice is 0.7 mg/kg. Death is accompanied by spasms due to respiratory paralysis; 0.04 mg/kg will influence respiration and will cause spasms.

14.1.2. Picrotoxin

Picrotoxin is a constituent of the seeds (*cocculus indicus*) of a climbing plant (*Anamirta cocculus* [as published]) widespread in Asia. The toxin's most active component is picrotoxinin.



(14.7)

These are colorless, needle-shaped crystals with a bitter taste (F about 200° C) which dissolve little in cold water but which are dissolved better in boiling water. The toxin is soluble in alcohol but not in ether and chloroform. Its aqueous solutions react neutrally.

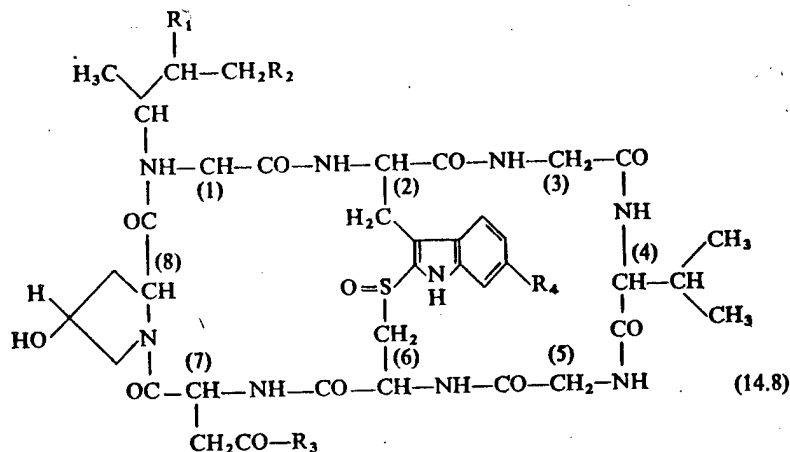
After oral consumption, one gets a burning sensation in the mouth. There is flow of saliva, followed by vomiting, and a feeling of thirst; the poisoning victim becomes dizzy, he experiences fear, is confused, and falls into a kind of somnolence. In addition there are delirium and cramps and the pupils are widened. The deadly poisoning terminates due to respiratory paralysis or exhaustion.

A protein-containing toxin is the active component of purple rose (the sea anemone *Actinia equina*). The chromatographically enriched product has an LD₅₀ of 33.3 µg/kg of body weight in rats when administered i.v.

The toxin has a hemolytic effect. Lung edema and internal bleeding were observed in the poisoned animals. Death is due to respiratory paralysis.

14.1.3. Mushroom Toxins

The toxin sources of most poisonous mushrooms today are known in terms of their structure. The phallotoxins and amatoxins are the most poisonous along with the active substances of green *Amanita phalloides* and its white relatives (*A. verna*, *A. virosa*). These are cyclic polypeptides which contain acid-amide-like aminocarbonic acids and, as shown by the constitution of the amino toxins, are arranged around an indole nucleus.



They contain among other things (-)-alanin, (-)-threonin, (-)-cystein, (-)-tryptophan. (-)-oxyprolin and leucines.

The phallotoxins are more than ten times less poisonous than the most poisonous amatoxins. According to Wieland, the most poisonous amatoxins include the following:

	R ₁	R ₂	R ₃	R ₄	LD ₅₀ (1) (i.p., Mäuse) mg/kg
I α-Amanitin	OH	OH	NH ₂	OH	0,3
II β-Amanitin	OH	OH	OH	OH	0,4
III γ-Amanitin	OH	H	NH ₂	OH	0,5
IV ε-Amanitin	OH	H	OH	OH	
V O-Methyl-α-amanitin	OH	OH	NH ₂	OCH ₃	0,2
VI Desoxo-α-amanitin	wie (I), ohne O am S-Atom (2)			(OCH ₃)	1,0

Key: 1--Mice; 2--Same as (I), without O on the S-atom.

V and VI are derivatives of natural toxins.

To obtain synthetically poisonous amatoxins, there is one prerequisite and that is that the eight amino acids of natural amanitin remain preserved as a ring which is divided between the amino acids (2) and (6) by means of a bridge, containing the indole ring, as sulfoxide or in the thioether structure. Amatoxins are synthetically demonstrable.

The phallatoxins, phalloidin and phalloin very quickly lead to serious liver damage while the liver and kidneys are attacked more slowly by the amatoxins.

Amanitin is a crystalline substance (F [melting point] 245° C). A quantity of 100 g fresh mushrooms will contain 10 mg phalloidin, 8 mg α -amanitin, and 5 mg β -amanitin.

The mushroom toxins are not decomposed in the intestine. They retain their activity after the mushrooms have been dried and boiled. In the organism they act as whole molecule or in molecule groups which are specially arranged in terms of space and structure.

Poisoning takes place after several hours of latency time and is expressed by vomiting, diarrhea, colic-like stomach cramps, accelerated breathing, and unconsciousness. Death occurs due to serious liver and kidney damage after 2-5 days.

The amatoxins can be compared to phosphorylated thiocholinesters in terms of their toxicity. Because they are hydrolytically and thermally stable, they are suitable as sabotage poisons above all to poison water, as well as essential and nonessential foods.

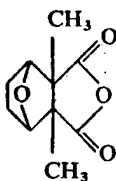
The active constituents of other poisonous mushrooms mostly involve alkaloids. The poison of fly amanita--muscarin--is an easily deliquescent crystalline mass (100 g of mushrooms will contain about 16 mg). Its LD₅₀ (i.v., mice) is 0.23 mg/kg. It reacts alkaline in aqueous solutions.

It was possible from one of the *Aspergillus* species (watering can mold) to isolate a somewhat less poisonous metabolite, called Viriditoxin, as a crystalline green substance (C₃₄H₃₀O₂₂, F 242° C). It is reported to have an LD₅₀ (i.p. mice) of 2.8 mg/kg.

14.2. Toxins of Animal Origin

14.2.1. Insect Poisons

Cantharidin (melting point 218° C) is the best-known and most effective insect poison.



(14.9)

It is a derivative of cyclohexane-dicarboxylic acid and occurs in the so-called Spanish flies (*Lytta vesicatoria*). The crystalline compound, which is only poorly soluble in cold water, is synthetically demonstrable. It is dissolved rather well in fats and oils.

The lethal dose for man is around 40-80 mg. Oral ingestion is followed by saliva flow, a burning sensation, the formation of blisters and scabs in the mouth (serious damage to mucosae, severe thirst, nausea, bloody vomiting, bloody stool and urine (hemorrhage), severe pains in the kidneys, in the urinary duct and in the bladder, uterine bleeding, and enlargement of the sex organ (priapismus). The discontinuation of urine discharge leads to severe kidney damage. Death is accompanied by cramps in the bladder-kidney region.

Dissolved in oil, about 0.1 mg will cause big blisters on the skin's surface; there is painful necrotic destruction on the mucosae.

Cantharidin is known as a homicide poison. It could be used as sabotage poison in fat-containing essential foods.

14.2.2. Snake Poison

About 300-400 types of snake poisons are known. If we add the poisonous sea snakes, the number goes up considerably. Snake poisons do not have a uniform composition and consist of a mixture of biologically highly-active polypeptides and proteins which can contain small quantities of alkali salts, magnesium, and zinc. They contain large quantities of albumin-splitting and fat-splitting ferments. With a few exceptions, it has hardly been possible to this very day to isolate the ferments from snake toxins in pure form although it has been able to determine their existence. Mixtures of small-molecular, ferment-free polypeptides or peptides are blamed for the enormous toxic effect; here one cannot rule out the possibility that the enzymes start and promote the action mechanism of these peptides.

In some cases it has been possible to determine as many as 20 aminoacids in snake poison. Typically for all of them is a very high cysteine content (up to 5.5 percent in dry poison) which is blamed for the toxic effect.

Because of the big differences in their compositions, snake poisons do not cause any uniform contamination picture.

Slotta subdivides snake poisons into three groups according to their effect.

Poisons with Neurotoxic Effect

They have an effect resembling curare paralysis and this effect is expressed in a paralysis of the respiratory musculature, leading to death due to respiratory arrest.

A typical snake poison in this group is neurotoxin, a small-molecular, heavy basic polypeptide from the Indian cobra (*Naja naja*), also known as Indian cobra toxin.

In addition to the effect on the peripheral nerve endings, these poisons cause central disturbances which affect both the brain centers and the respiratory centers; the poison of the rattlesnake, crototoxin, which contains highly toxic crotactin, will cause blinding among other things.

Toxins Acting on Circulation

There will be a blood pressure drop after contamination here due to the release of biogenic substances acting upon the circulation. Cobra toxins and the poisons of the vipers also have an effect on the heart.

Poisons with Local Effect

In the case of these poisons it is typical that they act upon the blood and tissue cells, leading to necroses and bleeding which will then appear at the bite places or at the places of penetration into the skin.

Raw snake poisons are clear or milky-cloudy, colorless or golden-yellow liquids which, if left standing for a longer period of time, will coagulate and they are well soluble in water. Because of their high water content, they are lyophilized. The dry substance is powdery and can be kept for more than 20 years without any major decline in toxicity.

The neurotoxin from the cobra has a molecular mass of about 10,000 (6,000), while crotoxin has 12,000 (18,000). Neurotoxin contains 13 aminoacids while crotoxin contains 18. The empirical formula for crotoxin is $C_{1230}H_{1776}O_{432}N_{328}S_{36}$.

The lethal dose of the dry substance of the poison of the rattle snake has been estimated at about 24 mg while it has been estimated at about 70 mg in the case of viper poison for man. Death depends on the dose absorbed and in case of small doses comes within 8 hours, in case of larger doses, within an hour.

The poisons of marine snakes are considerably more poisonous than those of land snakes. The lethal doses determined on mice are about 10 times smaller in the case of marine snake poisons.

An LD_{50} of 0.11 mg/kg i.v. and 0.5 mg/kg s.c. was determined for mice in the case of crotoxin or its main fraction. In the case of the toxin of *Naja naja*, the fraction, which contains the neurotoxin, has an LD_{50} of 0.295 mg/kg for rats in case of s.c. administration. An LD_{50} of less than 0.05 mg/kg, i.v., has been given for the α -toxin of cobraoxin. This is a simple polypeptide molecule and contains 61 aminoacid remnants.

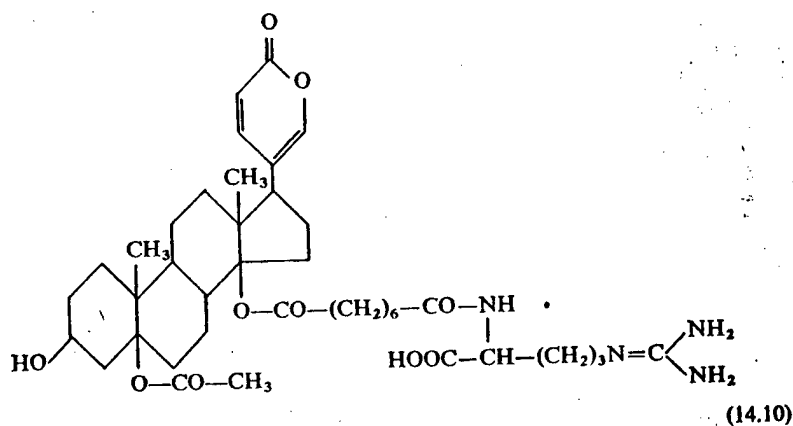
14.2.3. Scorpion Poisons

The toxins of tropical scorpions are particularly dangerous. The toxins are contained in the rear sting of the animal. They are easily resorped and they cause muscle cramps in the neck and chewing muscles, saliva flow, and lung edema after 2-3 hours. They are polypeptides. North American scorpion species above all contain neurotoxic components with molecular masses of around 15,000. In mice, the LD_{50} is 0.5 mg/kg. As much as 4 mg of dry substance can be obtained from one animal. About 200 guinea pigs can be killed with 0.5 mg of the poison from the North American thick-tail scorpion.

14.2.4. Frog Poisons

Various species of frogs secrete highly-poisonous toxins along with their skin secretions which have varying pharmacological-toxic effects. These are essentially toxins which have a very strong effect on the heart and those which have a neurotoxic effect. In recent years it has been possible by means of partial syntheses to make identical toxins. The poisons of frogs include batrachotoxin which is among the most poisonous substances of animal origin.

Bufotoxin and atelopitoxin are strong heart poisons. In 1943, Behringer provided the following makeup for bufotoxin, one of the most active components of the common toad:

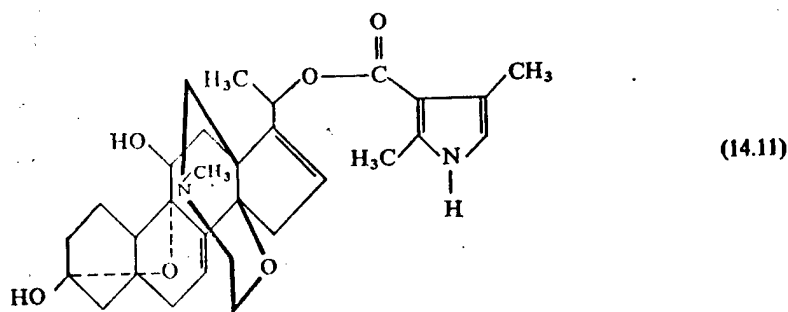


These are needle-shaped bitter-tasting crystals which melt at 204°C and are decomposed. The effectiveness of the toxin regarding the heart is comparable to that of the vegetable heart glycosides, strophanthin or scillaren.

The body resorbes bufotoxin very quickly. Poisoning leads to an increase in blood pressure, an increase in the heart rate, an urge to vomit, and cramps. Death is due to ventricular fibrillation. The lethal dose for cats, i.v., is 0.3 mg/kg of body weight.

The poison from the skin of frogs of the *Atelopus* family is more effective. A concentrate of the dialyzable atelopitoxin, which proved to be a strong heart poison, had an average lethal dose, i.v., of 0.016 mg/kg of body weight for mice.

Neurotoxic and cardiotox batrachotoxin:



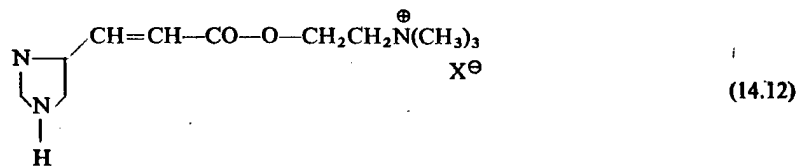
is the active substance of kokoi poison which is contained in the skin secretion of the Colombian arrow-poison frog (*Phyllotates aurotaenia*). In addition to batrachotoxin the poison contains isobatrachotoxin and a batrachotoxin A. The kokoi poison is a base which is soluble in halogenated alkanes and chloroform.

Batrachotoxin is a steroid alkaloid. It blocks the motor endplates. Death is accompanied by severe spasms and is due to respiratory paralysis. The average effective dose is reported to be below 0.5 $\mu\text{g}/\text{kg}$. The lethal dose for man, that is, LD_{50} , has been estimated at 2 $\mu\text{g}/\text{kg}$. In mice, the LD_{50} is 1.15-2.7 $\mu\text{g}/\text{kg}$; for batrachotoxin A it is given at 0.1-0.3 $\mu\text{g}/\text{kg}$.

14.2.5. Poisons from Marine Animals

The most poisonous toxins from marine organisms--tetrodotoxin and saxitoxin--are listed in the pertinent literature as potential toxin warfare agents. In recent years moreover a large number of toxic substances from various marine animals has been investigated and partly identified; these may be of military interest because of their toxicity. Depending upon their type, marine organisms produce toxins with widely differing composition, such as cholinesters, polypeptides, proteins, heterocyclic systems with a complicated structure, but also amins with a simple structure.

14.2.5.1. Murexin



Chemical name: Imidazolyl-4-propane-acid-cholinester.

Murexin is an imidazol derivative and is isolated from purple snails (Muricidae). It can be made synthetically.

Its pharmacological effect resembles that of other choline derivatives. Murexin excites the ganglia and blocks neural stimulus transmission. As a result of the polarization of the motor end plates, the effects are equal to those of the disturbance of ACh metabolism through ChE inhibition. Murexin is not hydrolyzed by ChE.

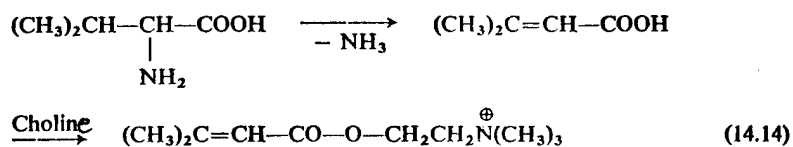
Murexin poisoning will lead to the paralysis of the skeletal musculature. The deadly outcome of contamination is the result of paralysis of respiratory musculature.

14.2.5.2. Seneziolylcholine



Chemical name: 3-Methylbutene-(2)-acid cholinester; β , β -dimethylacrylic acid cholinester.

Seneziolylcholine is isolated from the gastropods *Thais floridiana*. In them it is probably formed from valin and choline according to the following:



In alkaline solutions, seneziolylcholine is decomposed along with the formation of water-vapor-volatile acrylic acid.

The toxic principle corresponds to that of murezin. The toxin does not split ChE or it does so only to an insignificant extent.

14.2.5.3. Nereis Toxin

Nereis toxin is a compound related to liponic acid, 6,8-thiooctane acid (14.15) in which a dithioether is connected in ring-shape with a dimethylamino group and which has the following structure (14.16):



This is a very strong neurotoxin which occurs in the marine ringworm *Lumbriconeris heteropada*. Poisoning leads to a narrowing of the pupils, to the flow of saliva and tears, as well as to muscle contractions. The lethal dose, s.c., for rabbits is 1.8 mg/kg. Compared to other toxins, it is relatively high.

14.2.5.4. Additional Toxins from Marine Animals

Anglerfish toxin is secreted by *Trachinus draco* from the glands in the skin. Necrotic skin damage will result already from contact with the fish due to the pricks of the stings on the backfin. The organism very easily resorbs the poison. The general toxic effect is expressed by difficulty in breathing, a feeling of dizziness, profuse sweating, delirium, and cramps. Such contact poisoning very rarely leads to death. Undiluted, 100 percent $4 \cdot 10^{-4}$ cm³ of toxin will kill mice within 24 hours. As -60° C, the toxin can be stored for at least 2 years with glycerin additions. The poison is destroyed by alcohol, acids, and lyes.

Maculotoxin is a neurotoxin resembling tetrodotoxin and saxitoxin which is separated from the rear saliva glands of the squid *Hapalochlaena maculosa*. Respiratory paralysis and bradycardia were observed in rats after poisoning.

Sea Snake Toxins

Some species of sea snakes are more poisonous than land snakes. The *Laticanda* (*L. laticandata*, *L. colubrina*, *L. semifasciata*) species contain very strong toxins. The poison from the last-mentioned species contains three toxins, that is, erabutoxin a, B, and C. All three toxins contain 62 aminoacid remnants and four dithioether bridges. The toxins are crystalline, their molecular weights are around 7,000. Erabutoxin C has an LD₅₀ 0.13 µg/kg of body weight for mice. These toxins work in a manner similar to acetylcholine.

Palytoxin was isolated from a coelenterate (*Palythoa*) from the Zoanthidae family. It is a noncrystalline, white, very hygroscopic substance with a sum formula of C₄₁H₇₃NO₂₀. It is included among the most poisonous natural toxins. The chromatographically isolated toxin had an LD₅₀, i.v., of 0.15 µg/kg and, i.p., of 0.4 µg/kg for mice.

15. Synthetic Poisons

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15. Synthetic Poisons

In discussing natural poisons we were already able several times to point out that many of them are synthetically demonstrable and that a large number of their synthetic analogs are highly poisonous compounds. Basically, a separation would not be justified if one were to deny the origin of these compounds and especially the start of research in these fields. Investigations on toxins thus start with microbiology and with experiments designed to make them synthetically and then switch to chemistry. This accordingly applies to all other natural substances. The manufacture of synthetic poisons, and the manufacture of most chemical warfare agents, from the very beginning were connected with chemistry and chemical toxicology. Only later was it found that one or the other compound was an effective constituent of a naturally occurring toxin. This also applies to the fluorocarbonic compounds described here, more specifically, sodium- and potassium fluoroacetate, which are the toxic principle of *Dicephalatum cymosum*, a plant well known from South Africa. We also know that hydrocyanic acid, produced in industry on a large scale, occurs in about 300-400 different plants.

In this chapter we will therefore cover those compounds or groups of compounds which are synthetic compounds from this viewpoint. They are powerful poisons and as such they are suitable for military uses in poisoning men and useful animals, either in the form of sabotage poisons or, under certain circumstances, also as warfare agents in combat. The latter of course applies only to the organic compounds. Hardly any of the inorganic compounds mentioned has properties that would make it suitable as warfare agent in combat although experiments were also conducted along these lines.

15.1. Fluorocarbonic Compounds

The fluorocarbonic compounds were tested in several countries at the start of World War II for their suitability as CW agents. The first organic fluorine compounds had been made already before the turn of the century. Systematic work in this field of fluorine chemistry began about 50 years ago. There was a big upswing here after World War II. Fluorine chemistry is now used in plastics chemistry; its products are used in dyeing and textile aids, as fire-fighting and coolant substances, in metallurgy, as pest control agents, etc.

The high toxicity of certain organic fluorine compounds persuaded military chemical research in the imperialist countries to make such compounds and to test them for their usefulness as warfare agents. This was done above all in fascist Germany and in Great Britain and during World War II. As the choice was narrowed down, the chemists settled among others on hydrofluoric acetic acid methylester (15.1) and 2-fluorethanol (15.2).



The compounds selected in an almost ideal fashion meet the ideal requirements for sabotage poisons. They are stable and they are imperceptible; their mixability with water is partly good. They are highly toxic and they take effect only later because of the latency time. Both the analytical and their histological recognition is difficult, as is the treatment of contamination. This is why the investigations were directed at the possible use of these compounds as sabotage poisons to contaminate drinking water, food and fodder, pasture land and the like, which is what these compounds are suitable for.

15.1. Structure and Effect

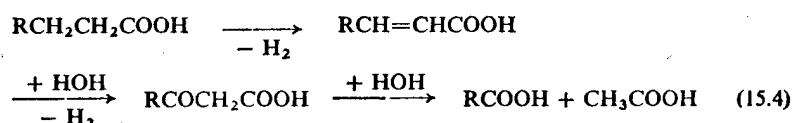
Organic fluorine compounds are toxic or nontoxic. The prerequisite for toxic activity is their behavior during hydrolysis or during oxidation. They are toxic if the organic fluorine compound is in a position, in case of biochemical reactions, to form hydrofluoric acetic acid, FCH_2COOH , or their ion. That can be acids, amides, acid halogenides, esters, alcohols, aldehydes, ether, and others. Saunders et al. found that they are very toxic only when we are dealing with compounds with the basic structure:



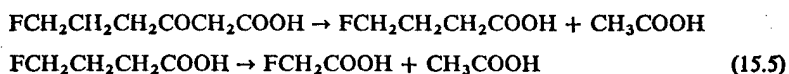
where n is an uneven number (see Table 15.1).

This observation applies to almost all organic fluorine compounds if they incline toward the formation of the radical $FCH_2CO\cdot$. Any substitution on the α carbon atom of this radical leads to a reduction or elimination of toxic activity even if we are dealing with a second or third fluorine atom.

The striking change in toxicity within a homologous series is compared to Knopp's theory of β oxidation of fatty acids in the organism where the ω fatty acids are gradually reduced to acetic acid.



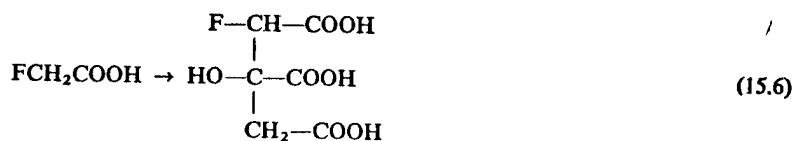
Organic fluorine compounds are reduced parallel to this β -oxidation.



Toxic hydrofluoric acetic acid is formed only in compounds where n is an uneven number. Compounds where n is an even number and those with branches [ramifications] are not reduced to hydrofluoric acetic acid. They are nontoxic, like 4-Fluor-2,2-dimethylbutane acid, $\text{FCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2$.

Because some organic fluorine compounds do not follow the rule of β -oxidation, other action principles are discussed.

It is now accepted as certain that the toxic principle of organic fluorine compounds is the conversion of hydrofluoric acetic acid into hydrofluoric citric acid.



This leads to the blocking of the tricarboxylic acid cycle. According to Peters (Proc. Roy. Soc. London, Ser. B. 139 (1951/52), p 943), there is an assumption that we have a competitive inhibition of the enzyme aconitase here which participates in the conversion of citric acid into iso-citric acid. Due to this blocking, the energy supply is interrupted and normal cell function is impaired.

The enrichment of citric acid furthermore causes the binding of calcium ions and this triggers neural and muscular disorders.

Carbon fluoride compounds can have an effect after inhalation after ingestion into the gastrointestinal tract, and, in the case of some of them, also after percutaneous resorption. Latency periods of 0.5-6 hours are followed by motor unrest, vomiting, saliva flow, and epilepsy-like spasms which are repeated periodically.

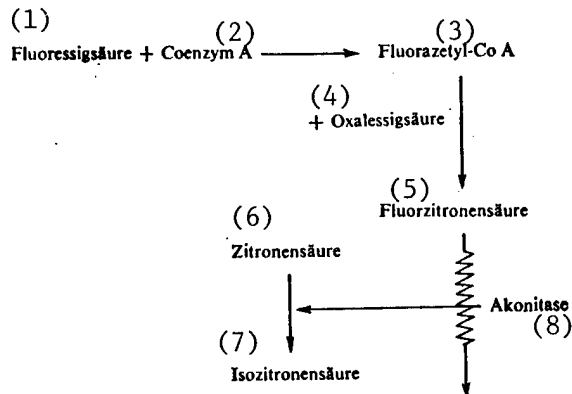


Figure 15.1. Inhibition of citric acid cycle by hydrofluoric acetic acid.
 Key: 1--Hydrofluoric acetic acid; 2--Coenzyme A; 3--Fluoroacetyl-Co A; 4--Ox-
 alacetic acid; 5--Hydrofluoric citric acid; 6--Citric acid; 7--Isocitric acid;
 8--Aconitase.

Additional symptoms are involuntary defecation and urination, possible loss of speech, and deep unconsciousness; voluminous secretion of fluids from the bronchial glands cause breathing difficulty. Death is due to cardiac arrest depending upon the concentration of dose after 3 hours or within 4-5 days; 75 percent of the poisoning cases end in death.

The toxicity of the compounds to be considered is roughly the same. Regardless of the type of compounds, the lethal dose for man is 2-10 mg/kg body weight.

The ω -hydrofluoric carbonic acid, their esters, and the ω -hydrofluoric alcohols are of special interest.

15.1.2. ω -Hydrofluoric Carbonic Acids



As we can see in Table 15.1 hydrofluoric acetic acid is the most toxic hydrofluoric carbonic acid. It is the toxically-active basic compound of hydrofluoric carbonic acid derivatives. It is colorless compound which forms needle-shaped crystals, which melt at 30° C, and which boils at about 167° C. Hydrofluoric acetic acid is easily dissolved in water and alcohol.

Its salt, sodium fluoroacetate (NFA) FCH_2COONa , a crystalline substance (melting point 76° C), is better suited as sabotage poison. It is soluble in water it is soluble only to a limited degree in alcohol.

Table 15.1. $F(CH_2)_n COOH$

n	Kp	F	LD ₅₀ (2) (Mäuse, i.p.)
	°C (Torr) ⁽¹⁾	°C	mg/kg
1	167 ... 168 (760)	31 ... 32	6,6
3	60 ... 62 (2)		0,65
5	193 (762)		1,35
7	145 ... 148 (10)		0,64
9		49	1,5
11		60 ... 61	1,25
17		69	5,7
.....			
2			60
4			100
6			40
8			100
10			58

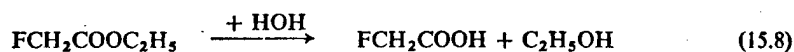
Key: 1--mm Hg; 2--Mice.

The analogous potassium compound was isolated from the previously mentioned African plant called Gifblaar (poison leaf). According to local experience, a few leaves of the plant are sufficient to kill sheep, goats, and cattle. Another plant, *D. taxicarium*, likewise at home in these regions, in its fruit contains ω -fluoro-oleic acid and ω -fluoroal-palmitin acid. The powdered seed is used as "ratsbane" rat poison. The plants were used by the local inhabitants at the time of colonial rule to poison wells, springs, and creeks and to make poison for arrowheads.

When taken orally, sodium fluoroacetate has a lethal effect on sheep at a rate of 0.7 mg/kg, for horses at 1.0 mg/kg, and for man at 2-10 mg/kg. In sheep, smaller doses did not produce any recognizable symptoms; only additional identical doses had a toxic effect.

Just a few drops of hydrofluoric acetic acid in a bucket of water will kill horses. Dogs, which ate the meat of poisoned horses, died likewise.

Free hydrofluoric acetic acid is made by means of hydrolysis of the hydrofluoric acetic acid ethylester in slightly alkaline medium according to the following:



15.1.3. ω -Hydrofluoric Carbonic Acid Alkylester



In the case of the hydrofluoric carbonic acid alkylesters it was also confirmed that those where n is an uneven number are toxic (see Table 15.2). The hydrofluoric acetic acid alkylesters, FCH_2COOR , and hydrofluoric acetic acid-2-fluoroethylester are of interest for military chemistry. The latter belongs to a group of compounds which, compared to the nonsubstituted alkylesters, revealed higher toxicity. These hydrofluoric carbonic acid 2-fluoroethylesters were made during World War II with the intention of combining the toxic properties of the ω -fluoroalkanoles with those of ω -hydrofluoric carbonic acid alkylesters.

Among the hydrofluoric acetic acid alkylesters, hydrofluoric acetic acid methylester was included among the smaller number of substances considered as potential warfare agents during World War II.

Hydrofluoric acetic acid methylester (methylfluoroacetate, MFA) is a colorless and odorless liquid which is dissolved in organic solvents, such as alcohol, petrolether and ether. Its solubility in water is 15 percent. The ester can be mixed in any ratio with sulfur Yperite and other warfare agents. It becomes rigid at about -32°C . Its vapor pressure at 20°C is 15 mm Hg; at the same temperature, the saturation concentration is $92 \text{ mg} \cdot \text{l}^{-1}$ ρ at 20°C $1.1744 \text{ g} \cdot \text{cm}^{-3}$.

The compound is chemically very stable. In an aqueous solution it is slowly hydrolyzed into identically toxic hydrofluoric acetic acid.



Table 15.2 F(CH₂)_n COOR

n	R	Kp	LD ₅₀ (3)
			Mäuse, s.c. ¹⁾
		'C (Torr) ⁽²⁾	mg/kg
1	CH ₃	105,5 (760)	15
3	CH ₃	78,5 (100)	(0,7)
5	CH ₃	70 ... 71 (1)	(1,6)
.....			
1	C ₂ H ₅	117 ... 118 (760)	15
2	C ₂ H ₅		200
4	C ₂ H ₅	56 ... 60 (16)	160
5	C ₂ H ₅	82 ... 84/14	4
7	C ₂ H ₅	145 ... 150/12	9 (1,75)
9	C ₂ H ₅	135 ... 138/10	10 (1,65)
10	C ₂ H ₅	140 ... 141/11	100
11	C ₂ H ₅	152 ... 153/11	20
.....			
1	FCH ₂ CH ₂	158 (760)	8,5
5	FCH ₂ CH ₂	103 ... 105 (14)	2,5
7	FCH ₂ CH ₂	128 ... 130 (13)	7
9	FCH ₂ CH ₂	145 ... 149 (12)	10

¹⁾ In Klammern: Mäuse, i.p.

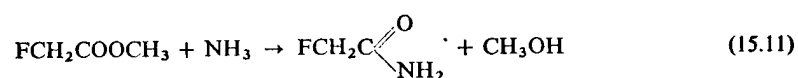
Key: (1) In parentheses: mice, i.p.; 2--mm Hg; 3--Mice.

A 15-percent aqueous solution at 23° C after 60 hours will only separate 2.5 percent of the total fluorine quantity and about 50 percent after 14 days. The cause of the slow hydrolysis speed can also be explained in terms of the heavily polar character of the C-F bond which counteracts a separation of the C-O bond.

Alkalis promote hydrolysis. In a 20-percent alcoholic alkali-hydroxide solution, it is possible to hydrolyze 50 percent after boiling 20 hours.

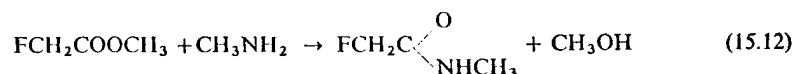
Acids do not promote ester hydrolysis so that neither the latter nor the alkali-lyes would be suitable decontamination agents.

Energetic reactions develop with aqueous, alcoholic, or etheric ammonia solutions. The following is reproduced:



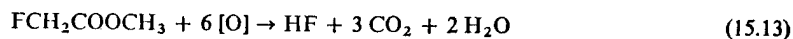
Fluoroacetamide which is likewise toxic, just like MFA. These are colorless crystals which melt at 108° C and which are soluble in water to the extent of about 15 percent.

In a similar manner primary amins form corresponding toxic N-alkylacetamides. α -fluoro-N-methylacetamide, which is contained in methylamide according to



is a crystalline compound (melting point 64° C).

The ester is split by strong oxidation agents. In this way we get carbon dioxide and hydrogen fluoride with chromosulfuric acid.



Potassium permanganate and nitrohydrochloric acid also have an oxidizing effect. Hypochlorite solutions do not react with MFA. Reactions materialize only with highly-active chlorine-containing compounds.

The LD₅₀ for rabbits is 0.25 mg/kg, i.v. The toxic effects starts in animals after 30-60 minutes. The experiments conducted by Saunders on himself did not cause any poisoning at concentrations of 1:10⁶. The dangerous concentrations are above 1:10⁵.

Fluoroaceticacidmethylester among other things can be made by means of reactions of chloroacetic acid methylester with potassium fluoride.

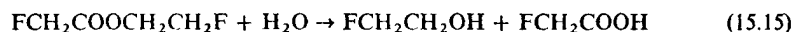


The higher ω -fluorocarbonicacid alkylesters are likewise colorless liquids which behave in a manner similar to MFA in chemical terms. As the C number increases, their water solubility and reactivity decline.

Fluoroaceticacid-2-fluoroethylester, $\text{FCH}_2\text{COOCH}_2\text{CH}_2\text{F}$, is a colorless, slightly odorous liquid (ρ at 20° C, 1.29 g cm⁻³) which becomes rigid at -25.4° C. It and its homologous compounds are extremely stable, they do not hydrolyze, and they react only with strong oxidation agents, for example, chromosulfuric acid. They form condensation products with alkalialcoholates.

The most toxic among the fluoroethylesters is ω -fluoropenta-carbonicacid-2-fluoroethylester. The higher toxicity of fluorocarbonicacid-2-fluoroethylester

compared to the nonsubstituted esters and also compared to fluoroethanol, is traced back to the two active fluorine groups in the molecule and not only to hydrolytic decomposition in the organism according to the following:



15.1.4. ω -Fluoroalkanols



The ω -fluoroalkanols are roughly just as toxic as the previously mentioned fluorocarboxylic acids and their esters (see Table 15.3). The lower fluoroalkanols are colorless liquids which are soluble in water. They are dissolved in organic solvents but not in petrolether.

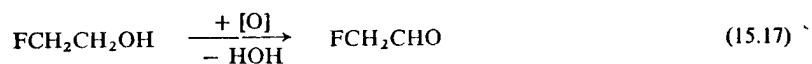
Table 15.3. $\text{F}(\text{CH}_2)_n\text{CH}_2\text{OH}$

n	Kp	(2) LD ₅₀ (Mice, i.p.)	
		°C (Torr) (1)	mg/kg
2	102 ... 104 (760)		10
3	126 ... 128 (700)		46,5
4	52 ... 53 (11)		0,9
6	85 ... 86 (14)		1,24
8	106 ... 107 (10)		0,6
10	136 ... 137 (15)		1,0

Key: 1--mm Hg; 2--Mice.

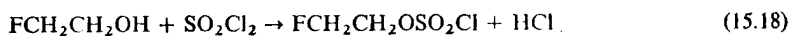
2-fluorethanol (FEA), $\text{FCH}_2\text{CH}_2\text{OH}$, can be mixed with water in any ratio. It becomes rigid at -43°C ; ρ at 20°C is $1.104\text{ g}\cdot\text{cm}^{-3}$.

It is stable in water, its acidic properties are more pronounced than in the case of ethanol. It is difficult to oxidize; only 6 percent fluorethanol are reproduced at 100°C with manganese (IV)-oxide and sulfuric acid:



Fluoroacetic acid develops with potassium permanganate; the yield is small.

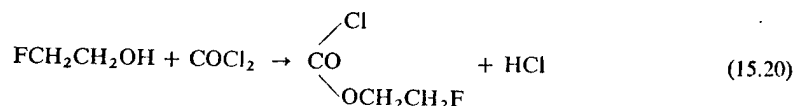
The reaction with surplus sulfurylchloride at 60° C gives us the likewise toxic chlorosulfonicacid-2-fluoroethylester which irritates the upper respiratory passages.



In case of excess fluoroethanol, we get the less toxic and nonodorous Bis-(2-fluoroethyl)-sulfuric acid ester.



Phosgene and fluoroethanol at 0° C produce the highly irritating chlorocarbonic-acid-2-fluoroethylester.



In the presence of pyridin, fluoroethanol reacts with phosphorus (III)-chloride to form Tris-(2-fluoroethyl)-phosphite, $\text{P}(\text{OCH}_2\text{CH}_2\text{F})_3$, a compound which is supposed to have a depressing effect on the CNS.

According to Saunders, after an exposure time of 10 minutes, 62 percent of the experimental animals (rabbits, rats, guinea pigs) are killed by a concentration of $0.29 \text{ mg} \cdot \text{l}^{-1}$ while 38 percent are killed by $0.14 \text{ mg} \cdot \text{l}^{-1}$. For the same exposure time, the LC_{50} [as published] at MFA is $0.1 \text{ mg} \cdot \text{l}^{-1}$ and for the fluoroaceticacid-2-fluoroethylester it is $0.05 \text{ mg} \cdot \text{l}^{-1}$. Contamination ended in death within 12 hours.

According to Dukelskaya, the time of death, as investigated on white rats, will depend on the dose (see Table 15.4).

Table 15.4.

Anzahl der Tiere (1)	Dosis (mg/Tier) (3)	Anzahl der toten Tiere (4)									über- lebende Tiere (7)
		nach 2 (5)	4	6	12	18	24	48	72	96h (6)	
25	0,08	-	2	5	1	2	6	2	1	1	5
30	0,1	1	2	16	14	5	8	-	-	-	-
20	0,5	2	6	-	4	-	7	-	-	-	-
10	1,0	1	1	1	3	3	1	-	-	-	-
5	2,0	1	-	3	1	-	-	-	-	-	-
15	5,0	2	-	10	-	1	2	-	-	-	-
5	10,0	-	4	1	-	-	-	-	-	-	-

Key: 1--Number of animals; 2--Dose; 3--Animals; 4--Number of dead animals; 5--After; 6--Hours; 7--Surviving animals.

Fluoroethanol among other things can be made by means of the condensation of hydrogen fluoride with ethyleneoxide in ethylether at 100° C or in the presence of catalytically acting traces of water according to the following:



15.2. Carbamates



Carbamates are mentioned several times in the literature as potential warfare agents (Sipri and others). These are the kind which have a relatively high toxicity against warm-blooded creatures. The oldest toxic compound in this group is Eserin (Physostigmin, 15.23), a natural poison whose structure has been known since 1925 and which was recognized as toxically active in the n-methylcarbamate group of NC-CH₃--COO-.

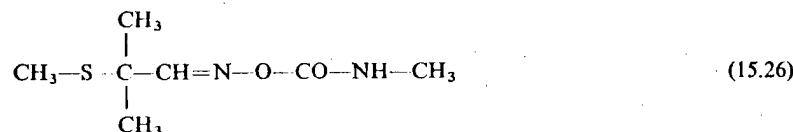
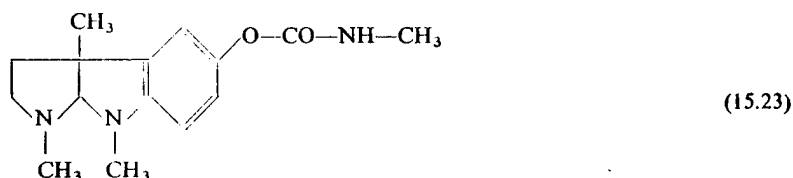
Carbamates inhibit cholinesterase and therefore are comparable to phosphororganyls in terms of their effect.

By means of carbamylation of the enzyme by deposit on its esteratic and anionic place it leads to endogenous acetylcholine poisoning due to blockage.

The dimethylcarbamates are colorless liquids or partly also solid substances which are little dissolved in water and gasoline but which are [illegible passage in photostat] easily dissolved in organic solvents such as alcohols, ketones, and ether. Without exception, the monomethylcarbamates of phenol and oxides are colorless crystals with a characteristic melting temperature. They are among the most toxic specimens.

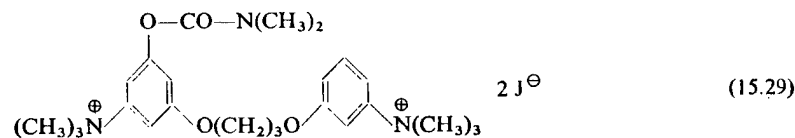
By way of example we might mention the following:

3,5-dimethyl-4-dimethylamino-phenylmethylcarbamate (15.24); LD₅₀ p.o. 15-63 mg/kg for warm-blooded creatures, in case of repeated contact, it acts through the skin; 3-(N,N-dimethyl-methylene-imino)-phenyl-methylcarbamate (15.25), LD₅₀ p.o. 20 mg/kg in the case of rats; 2-methyl-2-(methylthio)-0-(methyl-carbamoyl)-propionaldoxim (15.26), LD₅₀ p.o. 0.93 mg/kg for rats, 5 mg/kg for rabbits on the skin.

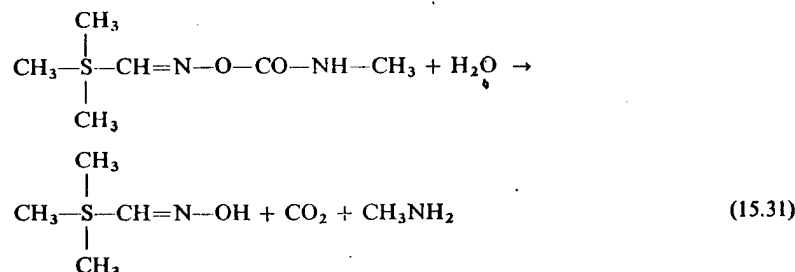
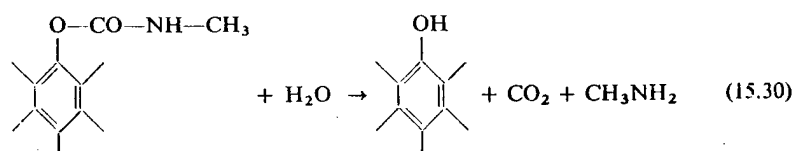


The last-mentioned compound can be used as insecticide only to a limited extent because of its excessively high toxicity for warm-blooded creatures. For this purpose it is granulated and covered with a water-soluble plastic layer to prevent contamination through the skin. It has a systemic effect and is oxidized into sulfoxide in the plant whose ChE-inhibiting effect is 10 to 20 times stronger.

The highest toxicity is encountered in carbamates which contain quaternary alkylammonium groups because they have functionally more favorable prerequisites when it comes to establishing reciprocal interaction with the anionic place on the ChE surface, something which is similarly the case with the quaternary phosphorylcholine derivatives, for example, the V-substances [annihilation agents]. The following among others are listed as potential warfare agents: 2-methyl-5-(trimethylammonium)-phenylmethylcarbamate (15.27); 5,N,N-dimethylcarbamoyl-1-methylquinolinium-bromide (15.28) and 1-(3'-trimethylammoniumphenoxy)-3-(3'-trimethylammoniumphenoxy-5'-N,N-dimethylcarbamoyl)-propane-di-iodide (15.29)

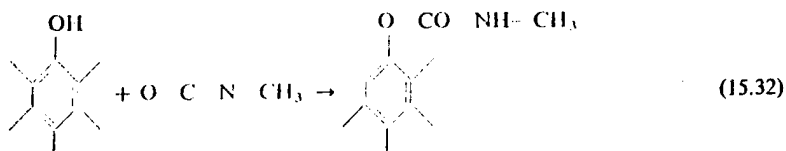


The carbamates are thermally stable up to 100° C but they are decomposed above 100° C, especially so in the presence of metal salts. With respect to alkalis they are unstable and in this respect they can be compared to Sarin. During alkaline hydrolysis, we get methyl- or dimethylamin, CO₂ and the pertinent phenol or oxim according to the following:



In neutral aqueous emulsions and suspensions they are sufficiently stable.

They can be made from the corresponding phenols by means of reaction with methylisocyanate according to the following:



in the presence of trimethylamin.

The pertinent literature contains corresponding references to the possible military uses of carbamates as warfare agents in combat. But they must be considered also as sabotage poisons.

15.3. Inorganic Toxins

Almost all inorganic compounds, so to speak, have certain physiological and pharmacological properties or they are partly highly toxic. That depends on the quantity, on the number of doses consumed, and, last but not least, on the manner in which the substance is introduced into the body. The toxic properties of inorganic compounds mostly are not as strongly pronounced as in the case of the organic ones. The number of toxins among the inorganic substances is much less than in the case of the organic ones. Compounds possible for sabotage purposes--to the extent that they are sufficiently soluble in water--are used in poisoning certain foods and drinking water.

Less soluble compounds for example can be used to poison flour, sugar, and salt. Arsenic III-oxide is suitable for poisoning flour used in making bread, while various mercury (II)- and lead salts are used to poison sugar, table salt, and other items.

Poisons to be used for contaminating essential and nonessential foods should unfold their toxic effect from the gastrointestinal tract. This means that adequate quantities must be resorbed by the gastrointestinal walls. If this is not so, such substances are very quickly eliminated again unchanged after peroral ingestion, for example, mercury (II)- and strontium compounds. There is a certain relationship between peroral toxicity of inorganic compounds and their solubility in water which is rather striking particularly in compounds of one element or an entire group.

One thing that is by no means of minor importance to peroral toxicity of inorganic compounds is their ionizability. The toxic activities spring from the ions of the compound. They could be both cations and anions which, in keeping with their specific properties, act upon the organs.

When plotting the toxicity values of the cations against the ordinal number of the corresponding element, we discover a periodicity of the toxicity which was examined in greater detail by Nofre and others (see Figure 15.2).

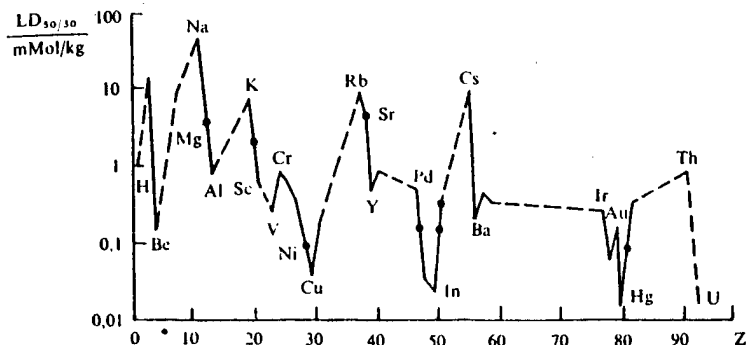


Figure 15.2. Toxicity of cations as a function of the ordinal number.

The relative nontoxic cations (maximums in the curves) are those of metals with negative normal potentials. The most toxic cations on the other hand are those of metals with a positive normal potential.

Table 15.5 shows the toxicity values of selected cations which were determined on male white mice, i.p., as LD₅₀ (after 30 days).

As in the case of the cations, the toxicity of the anions varies greatly. Table 15.6 shows the toxicity figures for selected anions (conditions as in Table 15.5). The sodium compounds of the specific anions were used here (based on Nofre et al.).

Table 15.5.

Cation	LD ₅₀ mg/kg	Cation	LD ₅₀ mg/kg
Na ⁺	1024	Co ²⁺ (1)	20,6
Sr ²⁺	503	Tl ⁺	20,4
Th ⁴⁺	206	Ag ⁺ (2)	13,9
NH ₄ ⁺	163	Zn ²⁺ (1)	11,7
Li ⁺	99,0	Ni ²⁺ (1)	7,93
Pb ²⁺ (3)	76,6	Hg ²⁺	3,92
Cr ³⁺	46,8	Cd ²⁺ (1)	3,71
Mn ²⁺ (1)	43,9	Cu ²⁺ (1)	2,86
Fe ²⁺ (1)	39,1	Be ²⁺	1,35
Ba ²⁺	35,5		

Key: (1) As sulfates; (2) As nitrates; (3) As acetates.

Table 15.6.

Anion	LD ₅₀ mg/kg	Anion	LD ₅₀ mg/kg
SO ₄ ⁼	2255	S ⁼	7,05
NO ₃ ⁻	2166	SeO ₃ ⁼	4,44
Cl ⁻	1576	TeO ₃ ⁼	4,22
ClO ₃ ⁻	467	AsO ₄ ⁼	4,17
ClO ₄ ⁻	448	CN ⁻	2,6
NO ₂ ⁻	106	Se ⁼	2,37
CrO ₄ ⁼	23,2	AsO ₂ ⁻	0,95
I ⁻	19		
SeO ₄ ⁼	7,15		

According to these figures, the compounds which might possibly be of military interest can be arranged in the following sequence in terms of their toxicity: NO₂⁻, F⁻, AsO₄⁼, CN⁻, AsO₂⁻.

In the case of possible sabotage poisons, such as HgCl₂, PbCl₂, and BeSO₄, the type of ion does not play any role. In these compounds, the cation is the active part. The use of chlorides, sulfates, nitrates, and acetates can be traced back to the good solubility of these compounds in water.

The properties of the following selected toxic inorganic compounds are generally known. They are potential sabotage poisons which can be used for this purpose in many different ways.

Compounds of the 1st Group of the Periodic System of Elements

Lithiumchloride

Although this compound is not very toxic, it can, when used in place of edible salt, cause severe poisoning symptoms. The Na⁺/K⁺ balance is upset by excessive consumption of Li⁺.

Copper (II) Compounds, Especially Copper (II) Sulfate

Copper sulfate has a lethal effect in man at doses of 10-20 g when taken orally. With the exception of copper canides, the other copper compounds are hardly any more toxic. Copper compounds are resorbed only slowly in the intestines. Poisoning mostly leads to vomiting whereby a large part of the nonresorbed copper salt is eliminated.

Compounds of the Second Group of the Periodic System of Elements

Beryllium Compounds

Beryllium cations reveal the highest toxicity among cations. Fluoride and acetate are suitable as poisons. Although nitrate is soluble in water, it would

hardly seem to come under consideration because of the acid reaction. Beryllium-acetate has a health-damaging effect already in small doses. It displaces magnesium and calcium from their protein compounds and 20 percent of all contamination cases end in death.

Baryum Compounds

Among the baryum compounds, only baryum chloride is suitable because of its good solubility in water and possibly also baryum nitrate and baryum nitrite. Soluble baryum salts are quickly resorbed by the intestine. Death can take place in just a few hours. A quantity of 0.2-0.5 g $BaCl_2$ will already lead to severe contamination while 0.8 g can have a deadly effect. It was reported that 2 g are absolutely lethal.

Cadmium Compounds

Cadmium compounds in the past frequently appeared by virtue of food impurities, especially in case of sour fruit juices which were kept in cadmium-containing cans. Cadmium ions act as strong ferment poisons. About 50-60 mg, taken perorally, are lethal for man. Cadmium compounds are quickly resorbed in the gastrointestinal tract.

Mercury Compounds

Here especially the mercury (II) compounds have a toxic effect. A quantity of 0.2-1.0 g of mercury (II) chloride, when consumed perorally, will cause death in man. If $HgCl_2$ is introduced into the empty stomach, poisoning can end in death within 36 hours. But it can last up to 3 weeks before death takes place.

Compounds of the Third Group of the Periodic System of Elements

Thallium Compounds

Chloride, acetate, and sulfate of thallium are quickly resorbed in the organism, even through the skin. They have been used frequently in the past for criminal intentions. For Tl_2SO_4 , the lethal oral dose is about 1 g. Deadly cases with 8 mg/kg of body weight or with 10-15 mg/kg body weight have become known.

Thallium compounds are cellular poisons. The poisoning cases usually last 2-3 weeks, while good health is restored 3-4 days after contamination.

Compounds of the Fourth Group of the Periodic System of Elements

Lead Compounds

Lead salts are easily resorbed by the mucosae in the mouth, by the respiratory tract, by the gastrointestinal duct, and even through the outer skin. They form insoluble complex compounds with albumin. Large doses of lead salts are absolutely deadly. The oral dose for lead acetate is about 5-30 g; 2-3 g will lead to serious poisoning.

Compounds of the Fifth Group of the Periodic System of Elements

Arsenic Compounds

Although all arsenic compounds are poisonous, only arsenic (III)-oxide or arsenious acid, possibly also arsenic acid--the latter above all in the form of its salts (arsenite, arsenate)--can be considered as sabotage poisons. Arsenic compounds were a poison that was in vogue for a long time. The lethal quantity for man in the case of As_2O_3 is about 60-120 mg. The toxicity depends on the poison's particle size. Arsenites are more toxic than arsenates.

Arsenic compounds are resorbed relatively fast in the gastrointestinal tract. They influence certain ferment systems and damage the capillaries. The contamination develops already after between 30 minutes and 3 hours, depending upon the quantity. Death occurs within 3 days due to respiratory arrest.

Antimony Compounds

Poisoning due to antimony compounds manifests itself in the same way as poisoning due to arsenic compounds. One substance which is particularly suitable as potential sabotage poison is so-called tartar emetic, also called potassium antimonyl tartrate, $\text{K}(\text{C}_4\text{H}_4\text{O}_6\text{SbO}) \cdot 0,5\text{H}_2\text{O}$, of which 100 mg have a lethal effect.

Inorganic compounds of other elements, with the exception of the fluorides, cyanides, and nitrites, could hardly be considered as potential sabotage poisons. Although the nickel and cobalt compounds are more toxic than perhaps the baryum and lead salts, they must be dropped because of their striking color. Among the salts, it is undoubtedly the cyanides which are the most toxic. Alkalicyanides and some others are easily soluble in water (basic reaction). They are just as toxic as hydrocyanic acid and they have the same effect as the former. About 110 mg NaCN or 145 mg KCN are lethal for man. Death takes place within 5 minutes in case of severe poisoning. The calcium balance is disturbed considerably (calcium precipitation) due to fluorides. A quantity of 250 mg sodium fluoride, when taken orally, will already lead to serious poisoning. About 5-4 g (as published) are reported to have a deadly effect. About the same deadly quantity has been given for sodium nitrite

The pertinent literature describes a vast number of poisoning cases with inorganic compounds due to conscious or accidental contamination.

[pp49-53]

16. Possible Use of Sabotage Poisons

Poisons can be used for sabotage purposes in very many different ways and their use can extend to tactical, strategic, or national economic objects. The purpose of their employment is to bring about death or the temporary neutralization of individual persons or groups of persons among military personnel and the civilian population. This may involve individual or mass poisoning. Sabotage poisons can be used both in the areas and during combat operations by subversives, special units, or aircraft.

Contamination targets can be water supply facilities, essential and nonessential foods, agricultural crops, livestock, and pharmaceutical as well as cosmetic products (according to Rothschild, especially foods no longer subject to further preparation, such as table fats, processed meat, dairy products, water and beverages as well as soaps and creams which have been overdosed or which have been poisoned by the addition of poisoned pharmaceuticals or by skin-damaging or percutaneously acting substances).

Rothschild believes that the strategic objectives of aggression would include the use of sabotage poisons for mass annihilation of combat units, of personnel at missile firing bases, of air force personnel, and of government and military command installations.

According to Schulzen ("Zivilschutz" [Civil Defense], Koblenz, 29, 1965, pp 264-271), acts of sabotage will be concentrated "mostly on large-scale drinking water contamination efforts as well as the most comprehensive possible destruction of useful animals." According to him, sabotage poisons "can be infiltrated already in peacetime by underground organizations with the help of false declarations and good camouflage. In case of war, sabotage teams can be supplied with sabotage poison by air. Sabotage agents can make highly toxic poisons if necessary from harmless substances by simple manipulation."

To poison drinking water, toxic substances should have suitable toxicity, water solubility, and hydrolytic stability.

As a relative criterion for suitability as sabotage poison, we can use the ratio between the substance's maximum solubility in water and the toxicity which is expressed as the degree of danger:

$$G_{\text{water}} = \frac{\text{Solubility in mg/l}}{\text{Lethal dose in mg/man (70 kg)}}$$

and which permits a certain estimate. The knowledge of the hydrolysis half-life makes it possible to judge the duration of contamination whereby it should be noted that this does not apply to possible inorganic sabotage poisons nor to most of the alkaloids which are stable in water. According to Table 16.1, VX, in addition to the toxins, has the highest quotient and is thus one of the most dangerous sabotage poisons.

Table 16.1. Degree of Hazard from Selected Warfare Agents and Poisons in Case of Drinking Water Contamination

Compound	G _{water}
Botulinustoxin A	10,000,000
VX	300,000
O-ethyl-S-(N,N-dimethylaminoethyl) methylthiolphosphonate	250,000
Sarin	100,000
Nicotine	20,000
Kolchizin	12,000
Hydrocyanic acid, cyanides	9,000
Amiton	5,000
Fluoroethanol, sodium fluoroacetate	1,500
Selenite	1,000
Arsenite, arsenate	1,000
Nitrogen Yperite (ammonia salts)	>800
Soman	<800
Thalliumfluoride	750
Strychnine sulfate	400
MFA, As ₂ O ₃	250
Fluoride, nitrite	200
Nitrogen Yperite	1-25
Sulfur Yperite	20
Lewisite	5

Sabotaging the water supply can be accomplished by contaminating water sources including the supply pipelines and the treatment plants, in the water reservoirs of untreated and treated water, and in the main lines.

The WHO in its 1970 report gave some examples of the possible effects of drinking water contamination: in case of contamination with Botulinustoxin A, the theoretical quantity for 20 million liters of water, assuming complete distribution of the toxin, is 0.04 kg and in case of uneven distribution, the six-fold quantity must be assumed. The initial concentration upon introduction into the line network should be around $0.05 \text{ mg} \cdot \text{l}^{-1}$. If 0.001 mg/person have a deadly effect, then 20 ml of water will contain a lethal dose. Because the first symptoms occur after 6-8 hours, the contamination can be extended to 6 hours. In a city with 50,000 inhabitants, where about 0.5 liter of water per person is consumed, it must be assumed that at least 60 percent (30,000 persons) will have ingested a lethal dose during that time.

To contaminate the same volume of water under identical conditions with LSD, we assume 10 kg or, in case of uneven distribution, eight times that quantity (about 80 kg). In the later case, the initial concentration is about $10 \text{ mg} \cdot \text{l}^{-1}$. If we use a psychosis-triggering dose of 0.25 mg/person as basis, then that dose will already be contained in about 2.5 ml of water. Because the first contamination symptoms appear after about 1-2 hours, the contamination of the water would have to be completed after 1 hour. Here again the same number of persons will be contaminated under certain circumstances.

It should be kept in mind that water consumption rises during hot summer days so that far larger quantities of toxin will be ingested by the consumers. Because of the latency time of such poisons, it is however hardly possible to warn the consumers, to flush or purify the pipeline system, or to take other measures to eliminate the contamination.

Similar considerations can be entertained regarding the contamination of table fats, meat products, and other items. Here, the hazard levels are much higher because most of the substances considered for sabotage actions are well dissolved in fats and oils. Because there are no hydrolytic effects here, the required poison quantities would seem to be roughly within the same ratios as in the case of water. Of course, that will depend on the type of food and the average consumption quantity.

Poisons which act through the skin or which damage the skin are above all suitable for contaminating surfaces, such as the surfaces of equipment, clothing, gear, etc. These will hardly involve substances which volatilize too quickly, which are perceptible by means of odor, or where contamination could be recognized on the outside. Contamination substances and other organic phosphorus compounds, certain carbamates, alkaloids, as well as aconitin, toxins, and under certain circumstances also warfare agents such as the Yperites are suitable for this purpose.

The contamination of agricultural crops is possible by means of systemically acting organic phosphorus compounds and also by means of carbamates. By means of the use of high-percentage formulas, it is possible to contaminate living plants, their fruits, etc., in such a manner that mass contamination can appear in man and useful animals after consumption. The utilization possibilities here again can be very many, for example, by spraying, by dropping toxic substances in water-soluble capsules, and by poisoning water reservoirs used in sprinkling the fields.

The possible use of warfare agents and toxic substances for sabotage actions requires complex protection measures, thorough inspection and monitoring, as well as the screening of potential sabotage targets (see R. Stoehr, MILITAERWESEN [Military Affairs], 12, 1968, pp 451-541).

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Plant-Damaging Warfare Agents (Phytotoxins)

[pp 55-57]

Plant-damaging warfare agents, so-called phytotoxins, were made by the United States during World War II for use against agricultural utilization areas. Among thousands of compounds studied at Camp Detrick, the U.S. Army's biological research center, chemists found the so-called agent 2,4-D, also called 2,4-dichlorophenoxyacetic acid (a) as a compound suitable for military purposes. In 1945, 450 t of that substance were made. The idea was to wipe out Japanese rice fields in the summer of 1945. But this did not materialize because of the planned use of nuclear weapons.

Plant-damaging warfare agents are phytoactive chemicals or formulas thereof with which agricultural crops are to be wiped out in order indirectly to damage human food production through shortages or to prevent natural camouflage through defoliation.

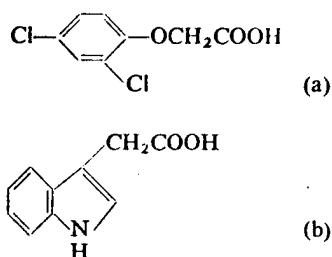
Herbicides, plant growth regulators, burning agents, and soil sterilization agents are of special importance here. Such agents have been used for a long time in agriculture and forestry as plant growth stimulators, to increase the yield, to improve the resistance of plants, for selective and total weed control, for defoliation or leaf removal from cultivated crops (to facilitate mechanical harvesting), for the production of seedless fruits, for eliminating underbrush, etc. On the civilian and military side this mostly involves the same groups of substances, although certain groups and substances are preferred for the individual sectors. The essential difference here consists in the fact that other "formulations" and larger quantities per surface unit are used for military purposes.

The plant's metabolism can be intensified by means of growth regulators. This is connected with an acceleration of physiological processes. Depending on the quantity of a phytoactive substance consumed, this can either help or harm the plant. Profound damage to the metabolism will lead to proliferations of the

plant cell tissue, to growth inhibitions, and other phenomena which lead to the plant's death.

Initial knowledge on natural plant growth substances goes back to the laborious work done by the plant physiologists Boysen-Jensen (1907), N. G. Cholodny, and Went (1924), Koegl (1934), S. S. Nametkin (1940), and others.

After it was recognized due to their work that these growth substances contained heteroauxin, synthetically easily accessible β -[indolyl-(3)2-acetic acid (b)], there was a solid foundation for further research in this field which was then also continued by military biologists in capitalist countries.



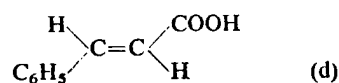
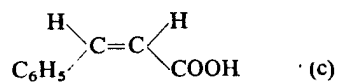
Phytotoxins were used for the first time between 1952 and 1954 on orders of the British High Command in Malaya (today Malaysia). The United States forces during their criminal 1961-1971 war in South Vietnam made comprehensive use of anti-plant warfare agents which caused ecological damage that can still not be estimated today. These agents were initially used with the intention of defoliating the jungle along strategically important traffic arteries and important objects and bases or to prevent any kind of plant growth and thus to impair the operations of the Vietnamese liberation army. In 1962, they began to use phytotoxins to destroy agricultural crop areas; rice fields, fruit plantations, and pasture land became favorite targets. According to official data, about 43 percent of the entire agricultural utilization area of South Vietnam (about 13,000 km²) and about 44 percent of the forests (about 25,000 km²) were poisoned in 1961-1970; in the process, the health of almost 1.3 million persons was damaged. According to American data, food for the nutrition of at least 850,000 persons per year was thus wiped out.

The use of plant-damaging warfare agents is a subject included in the strategic planning of the American military establishment for future warfare, including for war in Europe.

Some typical representative substances were selected from among the large number of phytoactive or phytotoxic chemicals and several of these were used by the United States in Vietnam and by Portuguese colonial troops in Angola.

These overwhelmingly involve photoactive compounds, apart from inorganic chemicals and their leaf-damaging agents, as well as those which in the molecule contain a ring-shaped grouping with at least one double bond. On the ring there

is a side chain with at least one carbon atom and one -COOH group or a functional group which can easily be converted into the carboxyl group. Besides, in some groups of compounds there seems to be a certain spatial relationship between the ring and the carboxyl group; this is the prerequisite for physiological effect. For example, among the phenylcarbonic acid derivatives, cis-cinnamic acid (c) is phytoactive and trans-cinnamic acid (d) is not.



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CSO: 8120/1304

DEVELOPMENT OF FLUID ADDITIVES FOR DEEP OIL, GAS DRILLING

Bucharest MINE, PETROL SI GAZE in Romanian No 3, Mar 82 pp 126-128

[Article by F. Popescu, Dr I. Ana, and M. Orosz]

[Text] The continued scarcity of hydrocarbons throughout the world has led, in the past few years, to intensified research to find new energy sources and to make better use of the existing ones.

In order to bring new reserves of hydrocarbons into economic circulation, in our country special efforts are being made to expand geological prospecting throughout the country, including the sea, especially prospecting at great depth (over 4,000 meters).

Under these circumstances, a number of extremely complex problems will have to be solved, such as:

--instability of the wellbore (collapse, excavation, choking of the hole) caused by the water-sensitive clay, by the strongly faulted, fissured and mineralized rock, by layers with abnormally high pressures (over 10^5 KPa) or with very low pressures (depleted);

--the intensified physical-chemical process caused by extremely high temperatures and pressures (175-250 deg C and over 10^5 KPa respectively) which degrade the rheological properties of the drilling fluid;

--increase in torque with increased depth;

--immobilized bit, drilling string or casing string;

--continuous increase in the content of corrosive gases (H_2S , CO_2) which, when coupled with high temperatures and internal tensions, cause an exponential increase in the speed of corrosion;

--higher circulation losses;

--slow progress at great depth and small diameter wellbores;

--mechanical and physico-chemical blockage of the productive formations;

--difficulties in pipe stringing, cementing, inspecting, and bringing the well into production.

One of the important aspects of well drilling and operation is the type and quality of the drilling, perforating, and packer fluids.

In addition to the traditional roles of the drilling fluid, such as:

--bringing the loose rock to the surface

--achieving the hydrostatic pressures necessary for control of the formation pressure

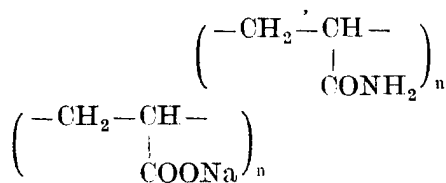
--cooling and lubricating the drilling equipment, etc.

these fluids must also help solve, or at least alleviate, the previously stated problems.

A number of additives are needed to provide drilling fluids which satisfy these requirements.

This article describes the additives currently used, classifies them by function, and points out their disadvantages for deep and for very deep drilling (over 4,000 meters and over 6,000 meters, respectively). It also describes the new additives for deep and very deep drilling developed during the past few years by research carried out at the Institute for Research and Design for Petroleum and Gases, at Cimlina, and shows the trends of future studies.

The additives presently used to prevent excessive penetration of the liquid phase into the strata and seal the walls of the wellbore have several drawbacks. Carboxymethylcellulose, for example, is thermally stable* up to 125-150 deg C and is relatively ineffective in the presence of electrolytes. Polyacryl amide and the polyacrylates are thermally stable up to 200 deg C, but are precipitated by calcium ions.



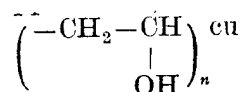
Research carried out at the ICPPG (Institute for Research and Design for Petroleum and Gases) has developed some wall sealants suitable for deep drilling, having high thermal stability, and which are effective in the presence of high concentrations of electrolytes.

*The temperature at which the polymers added to the drilling fluid lose their effectiveness.

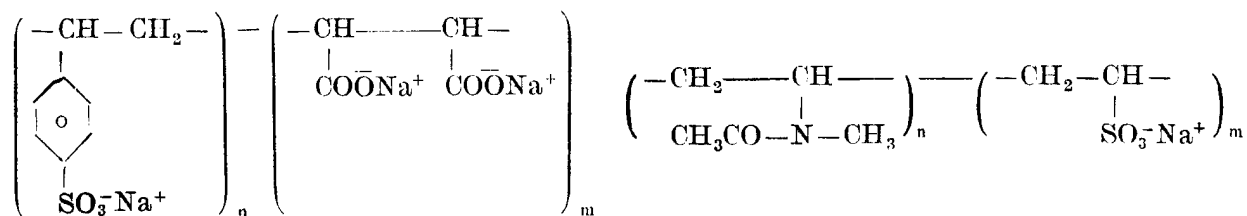
--FOREX (pregelatinized polysaccharide) is thermally stable up to 140 deg C and resistant to 300,000 ppm NaCl;

--LS-54 (sulfonated lignite) is thermally stable up to 200 deg C and resistant to electrolytes up to 300,000 ppm NaCl and 20,000 ppm Ca ions.

--APV (polyvinyl alcohol) is thermally stable up to 200 deg C and resistant to calcium ions contamination up to 50,000 ppm.



Continued research is being carried out for the development of some co-polymer-polyelectrolyte types of wall sealants of the sulfonated styrene-maleic anhydride type, of the N-vinyl N-alkylamide-vinyl sulfonic type, which are thermally stable up to 300-320 deg C and which are of special interest in drilling geothermal wells and 7,000 to 10,000 meters wells.



Fluidizers are additives which lower the excessive rheological properties of fluids caused by aggregation, by hydration and dispersion of clay particles, or by contamination with salt, gypsum, anhydrite. The currently used additives in this category are the ferro-chrome ligno-sulfonates with thermal stability up to 150-160 deg C, polyphosphates with thermal stability up to 80-90 deg C, and sodium humates which are thermally stable up to 175-190 deg C.

In order to provide a larger selection of fluidizing additives, the following were developed:

--chrome lignosulfonate (CLS) with thermal stability up to 170-180 deg C

--chrome-lignite (L₃) with thermal stability up to 200 deg C

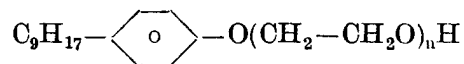
--a tannin based resin TAN-21, obtained by condensation and sulfonation, with thermal stability up to 130 deg C, which is of interest because it does not contain toxic chrome ions and causes less pollution.

Other developments include aluminum lignosulfate and potassium lignosulfate which are of interest for various types of fluids, especially for offshore drilling.

Research continues toward developing fluidizing additives of the methyl-sulfonic-lignosulfonic resin type which are low molecular weight polymers and are thermally stable up to 250-300 deg C.

Surfactants are additives which lower the surface tension of the filtrate and thus increase the production of an operating well. They are highly effective in forming emulsions (lead to light fluids used to lower circulation losses) and inhibit the hydration and dispersion of clays (by forming monomolecular films). Research has resulted in some effective surfactants with high thermal stability (200 deg C) such as the following:

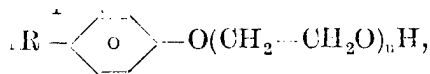
AAS--9 nonylphenol ethoxylate



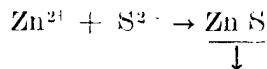
AAS--4 sodium alkyl-aryl sulfonate and sodium humate

EG--96 monoethylene glycol oxypropylate. These are effective additives and are not sensitive to calcium ion contamination. We should mention here that the previously used naphthenic soaps precipitate in the presence of calcium ions.

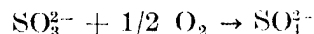
Further studies are being carried out to develop high molecular weight surface active agents with high inhibiting action of the alkyl and polyalkyl-phenol polyglycol type.



Developments in the area of corrosion inhibitors include a consumer (scavenger) of H_2S based on Zn humate and ZnCrO_4 . This additive precipitates the H_2S according to the reaction:



An oxygen consumer, based on catalyzed sulfites, scavenges the oxygen from the drilling fluid according to the reaction:



The advantage of these consumers of H_2S and O_2 is that they do not affect the rheological properties of the drilling fluids and have a higher thermal stability than the pelliculogen type inhibitors, based on amines.

Another problem to be solved is the jamming of the bits, drill strings, and casing strings because of "differential adhesion" to the deposits formed on the well walls by the higher hydrostatic pressure at the level of highly permeable strata. A newly developed additive, AD, consisting of a mixture of non-ionic and anionic surfactants has been developed for this purpose. The additive is dissolved in fuel oil or in a basic petroleum product, made heavier, and pumped into the area of the adhesion where it fissures the deposits and permits the fluid to penetrate in the cracks. By reducing the area of contact between the deposit and the drill string, by equalizing the pressures, and by providing lubrication, the drill string is being freed. There is a major advantage in using the above material: it helps recover the part of the wellbore which does not need to be re-drilled and also the drilling bit.

This product has been used in 20 wells and has solved 90 percent of the cases of jammed drill strings (at depths of 2,500 and 5,000 meters), as compared to 45 to 50 percent claimed in foreign technical literature).

A new lubricant, LFF-2, has been developed in order to reduce torque. It is based on a mixture of esters which do not influence the rheological properties of the drilling fluids, it is compatible with all types of drilling fluids, has thermal stability up to 150-175 deg C and reduces the friction coefficient between the drill string and the wall by 30-50 percent, depending on the type of drilling fluid.

Another additive, INHIB, has been developed to stabilize the water-sensitive clay rock. It consists of a mixture of macromolecular substances and dicromates, and, when added in amounts of 3-5 percent to water-based drilling fluids, reduces considerably the hydration and dispersion of clay particles.

Clay rock is not only water sensitive, but also has micro-fissures which make the wellbore much less stable. To help drilling through clay rock, a new product was developed, known as SGS, which consists of powdered bituminous asphalt, sodium humate and a non-ionic surfactant. This product seals the micro-fissures by providing a binder and also turns the clay into hydrophobic particles.

In the past few years, studies carried out at ICPPG-Cimpina have resulted in a number of additives, such as:

EMROM--emulsifier (calcium and sodium soaps of the fatty acids and surfactants)

ASAL--filtration diminisher (asphalt sulfoxidate)

OFP-82N--moisturizing agent

These additives have made possible the development of a new type of drilling fluid based on continuous phase petroleum products, fuel oil, in which a solution of CaCl_2 is dispersed as an internal phase.

The fluid thus obtained is called an "inverse emulsion" or an "oil fluid" depending on the water content (10-35 percent by volume or 5-10 percent by volume, respectively).

This type of drilling fluid has made possible the drilling of very deep wells under especially difficult conditions.

The well drilled and now in production at the Magurele formation has a depth of 5,920 meters, temperatures of 180 deg C and pressures of $10.3 \cdot 10^4$ KPa. The drilling fluid used was of the "oil fluid" type, with a density of 2,200 Kg/cubic meter.

At other wells, such as Margineni, Piscuri, Bustenari, the drilling proceeded normally up to depths of 5,000-5,500 meters, while using "inverse emulsion" drilling fluids. This would have been impossible to achieve with a water-based fluid.

At the moment, the well being drilled at the Baicoi formation is at 5,000 meters and "oil fluid" type drilling fluid will be used to drill down to 6,500 meters.

In addition to this type of drilling fluid, the newly developed additives have opened other possibilities.

The use of surfactants (AAS-9, EG-96, TENSROM) in the Bibesti formation has resulted in a fluid with a low solids content and this has led to considerably higher advance speeds.

Especially good results were obtained by developing and using the "INHIB-KCl" type drilling fluid, in the field. In addition to the 3-10 percent KCl, this fluid contains the INHIB, EG-96, etc. additives. The performance of this type of drilling fluid comes close to that of the "inverse emulsion" fluid (this has been proven in the field in several wells, including offshore drilling). This development should result in the gradual replacement (where possible) of drilling fluids based on petroleum products).

In conclusion, we feel that, as a result of our own research at the drilling fluids laboratories at the ICPPG, Cimpina, we have developed additives and drilling fluids which have made possible the drilling of wells under most difficult circumstances, at depths exceeding 6,000 meters, and also helped find rapid solutions to major difficulties which occurred in these drillings.

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INCREASED PRODUCTION OF SOLAR COLLECTORS URGED

Bucharest SCINTEIA in Romanian 9 Apr 82 p 2

[Article by Elena Mantu and Corneliu Cirlan]

[Text] During the current five-year plan and until 1990, as stipulated in the decision of the recent plenary session of the central committee of the RCP regarding the fulfillment of the electric power production program, the contribution of new energy resources will have to increase in the country's energy balance. Among these new sources, solar power is of immediate practical value, and is an area in which research and applications are well on their way.

Without delving insistently on the efficiency of exploiting this natural source of energy, let us look at one figure: 260,000 tons of conventional fuel (cc), whose oil equivalent would cost nearly 50 million dollars. This is the amount of primary energy that must be saved during 1985 by exploiting solar power. In order to achieve these savings, 475,000 housing units, hotels, motels, camping areas, and washrooms in many enterprises must be equipped with solar water heating units. At the same time, plans are being made for water heating installations for technical purposes in industrial units and animal raising farms, as well as for obtaining hot air to dry fruits, grain, wood, construction materials, and so on.

What major types of solar collectors are presently offered by research and production?

To be sure, the three types of solar collectors have each their advantages and disadvantages, because we are still beginning to manufacture them. The current problem is to intensify the fabrication of those that have the best technical performance and economic efficiency.

What do we learn from discussions with specialists? Researchers at INCERC (Research Institute for Constructions and Construction Economy) and ICSITEEMR (Institute for Scientific Research and Technologic Engineering for Power Equipment and Hoisting Machinery) estimate that the Sadu collector, which received a prize at the Moscow Inventors and Innovators Show in October of last year, certainly has the highest energy yield, a longer life than other types, and a broader field of applications (in installations that are large and small, simple and complex, with thermal siphoning, and without pumps); the collector is easy to manufacture, easy to install, and easy to maintain. Its disadvantage is that it requires about 13 kg of

Specifications	Sadu aluminum plate collector	Alexandria collector	Frigocom collector
Weight	59 kg	70 kg	62 kg
Aluminum consumption	13 kg	3 kg	--
Steel consumption	17.87 kg	42 kg	45 kg
Energy contribution	187 kgcc/yr	120 kgcc/yr	122 kgcc/yr
Price	2226 lei	1769 lei	1769 lei

aluminum, an energy intensive material; but the specialists have already found ways to reduce this consumption of aluminum. The characteristics of the Alexandria and Frigocom collectors are similar. The difference between them is only that the Frigocom unit does not use aluminum, that the coil is protected against corrosion, that it can also be used directly without a heat exchanger, and therefore with higher reliability, and that it has a constant yield which does not depend as much on the amount of sunshine, which means that it can also operate well in locations which are less sunny or receive diffused light.

Does the use of these two types of collectors lead to any savings? Some options are based on the fact that aluminum is a metal whose production requires a large amount of energy, and that it must not be used unless other solutions are not available. A wise attitude to be sure! But in the opinion of the specialists, the use of aluminum in solar collectors must be analyzed more thoroughly and considered more carefully, because calculations have shown that in order to obtain a given amount of power, 2 square-meters of Sadu collectors correspond to 2.60 square-meters of Alexandria ones. In this case, under comparable conditions, the energy included in the material used to fabricate the collectors is 246 kgcc for the Sadu type and 256 kgcc for the Alexandria. Consequently, no savings of primary energy result from the use of steel collectors instead of aluminum ones. And one of the advantages of the aluminum collectors is that they have a significantly longer life and reduce specific investments. Therefore, still under comparable conditions, the energy incorporated in aluminum collectors is recovered through the exploitation of solar power in only 1.6 years, compared to 2.1 years for the Alexandria type.

We have looked at the operation of the two types of collectors, the Alexandria and the Frigocom (made out of steel). At the Bucharest Enterprise for Tooling and Spare Parts, 324 Frigocom panels were installed last summer on the roof of one building. During the short period of its operation last year, the installation supplied hot water for the needs of the enterprise, for a savings of 10 tcc. During this year, it is estimated that its use for the entire optimum sunny period (April to November) will lead to a savings of 41 tcc. In practice, the installation produces more hot water than the needs of the enterprise, and a search is being conducted among neighbors for an eventual user of the surplus. As we have observed, the collectors survived the winter well, did not rust, and since the glass is well washed by a simple rain, required little maintenance.

During the same period, 254 Alexandria collectors were installed at the Energoreparatii enterprise in Bucharest. It is estimated that the use of this installation has saved 13.2 tcc in one year. How did it fare during the winter? All the panels, made of primed sheet metal, have rusted to some degree or other. One more winter and no one knows what will be left. Many of the panels have become

dulled (oxidation of the aluminum reflectors), thus reducing the installation's efficiency. The glass panels are not water tight, and the steel tubing coil is oxidized in places, with the rust staining the reflector. The situation is similar at other units that have this type of collector.

What is the producers' position in all this?

Eng Gheorghe Dorin Vieru, director of the Frigocom Enterprise: "We were asked to reduce the price of our collector, and found ways to bring it to the level of the one made by Alexandria, while retaining the operating specifications of the product. We could reduce the cost of the collector even further, but when the price was approved we were assigned a profitability of 19 percent, which in fact does not reflect the real efficiency in the fabrication of this product. We are prepared and have organized manufacturing lines for at least 40,000 collectors per year."

Chief Engineer Zoie Popescu, at the Alexandria Enterprise for Equipment and Accessories: "Since 1977, when we began the fabrication of solar collectors--as a national specialized enterprise, we have strived to assure a constant improvement in our products. We accepted the recommendation of specialists to improve the anticorrosion protection of our collectors, and we took the necessary steps without increasing production costs. We could sell the panels at a lower price, but we were assigned a profitability of 16 percent over production costs, which in our opinion is exaggerated. If we had orders (which unfortunately we do not), we could produce 200,000 collectors per year."

These are the opinions of specialists and our findings. We have raised the question of solar collectors, because a recent decision of the specialized organs in the State Committee for Planning, based on the good intention to guide the fabrication of these installations, stipulates that Alexandria solar collectors must be used in 1982, since the Sadu collectors are no longer made due to their high consumption of non-ferrous metals and their high cost. But as we have seen, this is the type of installation that has disadvantages compared to the others. That is why, echoing the position of the specialists, we propose the organization of a meeting of decision makers with specialists in research, planning, and production, and with users as well, to thoroughly analyze the existing solutions, starting with the general interests of the economy and the concrete possibilities of manufacturing, while taking into consideration the need to place these units on foreign markets. The adoption of a decision must of course also include the idea, which we deem a good one, that the fabrication of solar collectors should become the task of several enterprises, especially since the implementation objectives for these installations are very large and must be fulfilled in a very short time.

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CURRENT STATUS OF MICROPROCESSOR PRODUCTION

Bucharest SCINTEIA in Romanian 9 Apr 82 p 3

[Article by Vlaicu Radu]

[Text] The most indicative picture of the technologic explosion of recent years in the electronics field seems to be the one painted by a specialized institute, which pointed out that if the revolution in the electronics industry had occurred in the automotive industry, a Rolls Royce would cost five dollars, and it would be possible to cover 500,000 km at 500 km/h with a single liter of gasoline. The progress in electronics is a truly unique phenomenon in the history of technology. Moreover, in predicting the development trends in this field, some experts believe that everything that has already happened is only a prologue, and that electronics will remain one of the most important and dynamic technologies of modern civilization.

The development of semiconductor production and miniaturization technologies have been decisive factors in the evolution of electronics. Microelectronics--the fabrication and use of highly miniaturized electronic circuits--is today the most representative domain in the evolution of present electronics. The level of miniaturization currently practiced in the microelectronics of large scale integrated circuits available on the market, places more than 10,000 transistors on a silicon wafer with an area of 50 square-mm, and laboratories are working on structures which have more than 100,000 components.

Dr C. Bulucea, director of the Research Institute for Electronic Components, told us what these figures mean in physical terms: "If we were to miniaturize a newspaper page which contains 35,000 characters, at the same level scale as large scale integrated circuits, we would have to engrave it without any defects, on the surface of a postage stamp; the engraving would have to be done with letters in relief, precisely defined, and colored in seven colors, one of which would have to be metallized! If we were to work at the scale of very large scale integration, the entire newspaper could be engraved on the same area. Although it seems difficult to believe, such things are entirely possible, since the current technology disposes of an arsenal of material processing techniques, which properly used, can lead to the production of structures that can be engraved on silicon with the dimensions and characteristics described above."

Perhaps the most spectacular achievement of the past ten years in the area of highly integrated circuits, is the microprocessor, which is essentially a central computer unit in the form of a single integrated circuit. In its structure, the microprocessor includes over 5000 transistors implanted on a silicon area of approximately 20 square-mm. By adding integrated circuits for memory, interface circuits, and so on, to this central computer unit, it is possible to build a complete computer system called a microcomputer, whose data processing capability is that of a conventional closet-size computer, but whose dimensions are those of an attache case. In fact, the complete list of microprocessor applications is for the time being limited only by our imagination. Microprocessors are being built today, which can evaluate and direct complex processes performed by robot machines, without manned intervention and placed at man's service.

Remarkable in this respect are the foresight and understanding of this field's future on the part of our party's leadership, and of its secretary general, Nicolae Ceausescu, whose constant attention is directed toward the evolution of Romania's electronics. It is entirely natural that the development of microelectronics, including the production of microprocessors in Romania, would be considered as tasks of the greatest importance for the electronics field in the Program-Directive for Scientific Research approved by the 12th Party Congress. We have presented this review of an unprecedented revolution in the history of technology, not only to show the importance of the impact of science and technology on the development of electronic components, but also to provide a reference point for assessing the efforts that our country makes in the electronics field.

The production in Romania, in the near future, of large scale integrated circuits, including microprocessors, is taken by our specialists as a highly responsible task, because even though microprocessors have insignificant weights and dimensions (they weigh less than 10 grams), they constitute a major investment and concentration of talent. But as Dr Bulucea points out, while the advantages deriving from the use of microprocessors are well-known and publicized, it is less well known that their fabrication requires advanced-technology, computerized (some in fact, with microprocessors), special installations and equipment, produced only by a few foreign companies, which operate only in areas with temperature, humidity, dust-free, and vibration-free conditions that have so far never been achieved in any branch of our national economy. Moreover, our engineers are handicapped from the start by the export limitations of some countries which have equipment and technologies specific to the microelectronics industry. In this situation, the manufacturing and use of microprocessors in our country will have to be handled through the parallel and combined efforts of applications specialists and semiconductor specialists: while the former carry out projects and build prototypes with imported components, the latter create the necessary materials foundations, following which they will design and produce the much awaited microprocessors.

But in addition to electronics experts, the fulfillment of this objective requires the active and efficient support of the other sectors of the economy. Microelectronics is a technology of perfection, which demands the acquisition of advanced techniques in chemistry, metallurgy, machine construction, and so on, all of which will have to assure the domestic production of the ultrapure and special materials needed by this industry.

Given the capabilities of our specialists, and the investment support provided by the state as part of the priority microelectronics program, the promise made to the secretary general by the leadership of the Microelectronica Enterprise, to produce the first large scale integrated components as early as 1982, is a realistic one.

The responsibility of all involved in the completion of this objective is enormous, if one considers the fact that the potential of the Romanian industry can be exploited with maximum efficiency only by incorporating on an increasingly broad scale, automated and computerized installations that have evolved at the present level of electronics throughout the world.

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