Ferruccio Trifirò
Member of Scientific Advisory Board of OPCW

THE TWO FACES OF ARSENIC COMPOUNDS UNDER CONTROL OF OPCW AND REACH

Compounds of arsenic can be used to produce chemical weapons and other products which can be cancerogenic cat. 1A, therefore these products on the market must be under control. At present arsenic compounds are under the control of OPCW and ECHA. In the past, the main use of arsenic compounds was for pesticides production; now it is for electronic, glass production and metallurgy.

At present arsenic compounds are under the control of both the Organization for Prohibition of Chemical Weapons (OPCW) and the European Chemical Agency (ECHA), this last for the application of Reach regulation.
Arsenic is the 20th most abundant element in the earth's crust, 14th in the seawater, and 12th in the human body and is a component of more than 245 minerals.
As a mineral it is present as oxide, sulphides together with other elements (Fe, Cu), diarsenic disulphide of copper, nickel, lead, cobalt, and other metals, and arsenide (Ni arsenide etc.). The production of arsenic in the world, expressed as amount of As_2O_3 produced, is about 55,000-60,000 t/y, 50% is coming from China, then from Chile, Marocco and Peru and, in smaller amount, from many other countries (as Belgium etc.) [1, 3].

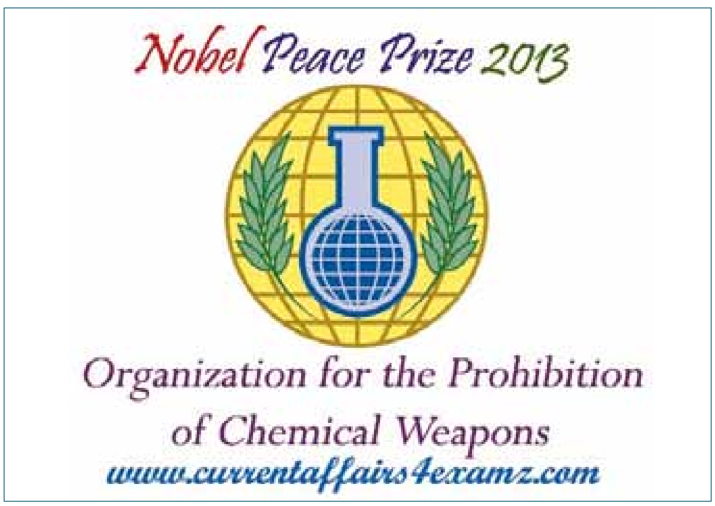
The two faces of arsenic compounds

Arsenic has been known and used in Persia and elsewhere since ancient times. Inorganic arsenic compounds were widely used as pesticides from mid 1800s to mid 1900s and in medicine; up to the 1970s about 80% of the consumption of arsenic was for agriculture purpose. At present, agricultural use of arsenic is declining, compounds of arsenic are used commercially and industrially as alloying agents in the manufacture of transistors, lasers and semiconductors, as well as in the processing of glass and metals. Arsenic has proven to be potentially useful in cancer treatment and could show some promise in the ongoing battle against cancer.
The negative aspects of arsenic compounds are the following:
1) all the arsenic compounds are cancerogenic cat. 1A (it is proved that they are cancerogenic for humans);
2) lewisite is a well known chemical weapon composed with arsenic, acting as a vescicant (blister agent) and lung irritant;
3) during the Vietnam War the United States also used Agent Blue, a mixture of sodium cacodylate and dimethyl arsenic acid, as a herbicide;
4) there is a strong contamination by arsenic compounds of ground water especially in China, Nepal, India, Bangladesh, Mexico and Argentina. This poisoning is a world wide problem, but this pollution is not due to the use of arsenic based products, but mainly from con-

taminations due to the fact that arsenic compounds are byproducts in many industrial processes, such as coal combustion and several metal refining and present volcano emissions.

Arsenic compounds under control of OPCW

Each country that belongs to OPCW must destroy all chemical weapons it owns or possesses, as well as all chemical weapons it may have abandoned in another country. It must destroy facilities it owns or possesses which were involved in the production of chemical weapons [4-7]. Several countries have declared chemical weapons, amounting to nearly 70,000 metric tones of toxic agents in 8.6 million munitions and containers. The biggest arsenals that must be destroyed are in Russia and United States. Member countries must take care that the destruction process cannot harm people or the environment. Also OPCW regularly inspects all former chemical weapons production facilities declared by Member States in order to verify that they are all shut down and destroyed, or converted for peaceful purposes. OPCW is additionally required to monitor the destruction of chemical weapons that are old or deteriorated or that were abandoned by one country on the territory of another. 81.71% of the world's declared stockpile of 71,196 metric tons of chemical agent have been verifiably destroyed. 57.32%, of the 8.67 million chemical munitions and containers covered by the CWC have been verifiably destroyed. From Entry into Force of the CWC (April 1997) until 09/30/2013, OPCW has conducted 5,286 inspections on the territory of 86 States Parties, including 2,731 inspections of chemical weapon-related sites, 228 chemical weapon-related sites have been inspected out of the total declared, 100% of the declared chemical weapons stockpiles have been inventoried and verified and 100% of the declared chemical weapons production facilities have been inactivated. Another objective of OPCW is to control all chemical productions in order to avoid that they can be transformed to produce chemical weapons.



The Nobel Prize for Peace 2013 was awarded to the Organization for the Prohibition of Chemical Weapons "for its extensive efforts to eliminate chemical weapons".

The decision by the Nobel Committee to bestow this year's Peace Prize on the OPCW is a great honour for our Organisation. We are a small organisation which for over 16 years, and away from the glare of international publicity, has shouldered an onerous but noble task - to act as the guardian of the global ban on chemical weapons that took effect in 1997. That year, a hundred-year effort was crowned with success as the Chemical Weapons Convention entered into force. Our organization was tasked to verify the elimination of chemical weapons from the world and to encourage all nations to adhere to this hard-earned norm. We have since then worked with quiet determination to rid the world of these heinous weapons - weapons which have been used to horrific effect throughout the twentieth century, and, sadly, in our own time too. Events in Syria have been a tragic reminder that there remains much work yet to be done. Our hearts go out to the Syrian people who were recently victims of the horror of chemical weapons. Today we are engaged in work which is meant to ensure that this atrocity is not repeated. Never in the history of our organisation have we been called on to verify a destruction program within such short timeframes - and in an ongoing conflict. We are conscious of the enormous trust that the international community has bestowed on us. Working to realize the vision of a world free of chemical weapons, we rely on the expertise, professionalism and dedication of our staff - qualities that have been forged through a solid record of achievement. This would clearly not be possible without the steadfast support and commitment of our States Parties. The recognition that the Peace Prize brings will spur us to untiring effort, even stronger commitment and greater dedication. I truly hope that this award, and the OPCW's ongoing mission together with the United Nations in Syria, will help broader efforts to achieve peace in that country and end the suffering of its people.

The director general of OPCW
Ahmet Üzümcü

The chemical products have been divided in three classes.

Schedule 1 chemicals include those that have been or can be easily used as chemical weapons and which have very limited, if any, uses for peaceful purposes. Some Schedule 1 chemicals are used as ingredients in pharmaceutical preparations or as diagnostics. as a calibration standard in monitoring programmers for paralytic shellfish poisoning, and are also used in neurological research. Arsenic chemical weapons compounds have been employed as a bio-medical research tool and they are usually produced and used for protective purposes, such as for testing CW protective equipment and chemical agent alarms.

Schedule 2 chemicals include those that are precursors to, or that in some cases can themselves be used as, chemical weapons agents, but which have a number of other commercial uses (such as ingredients in resins, flame-retardants, additives, inks and dyes, insecticides, herbicides, lubricants and some raw materials for pharmaceutical products).

Schedule 3 chemicals include those that can be used to produce, or can be used as, chemical weapons, but which are widely used for peaceful purposes.

In Schedule 1 there are the following compounds of arsenic: Lewisite 1 (2-chlorovinyldichloroarsine); Lewisite 2 (bis(2-chlorovinyl)chloroarsine); Lewisite 3 (tris(2-chlorovinyl)arsine).
In Schedule 2 it is present arsenic trichloride. Sources from China revealed that arsenic residues from chemical weapons that Japan used during World War II have not been properly disposed of and are still on Chinese soil. There have been calls for the toxic materials to be sent back to Japan, as it is feared that it could leak into the soil and cause health issues.
To have an idea of interest of science about chemical weapons we shall report some informations about lewisite. In scientific literature under the word "lewisite" are present 1,146 references from 1949 to 2013, in particular in 2004-2005 there are 35 references.
Within these 35 references 17 papers are on analytical aspects, 11 papers on biomedical aspects and 7 papers on decontamination.

Moreover there is another group of products under control, the so called *Discrete Organic Chemicals*, whose production plants could be used for production of chemical weapons.

Arsenic compounds under Reach

ECHA, the European agency for chemistry has evidenced substances called SVHC (Substances with Very High Concern) [8, 9], which are those with several negative properties for humans, animals and environment: carcinogenic or mutagenic or toxic to reproduction (CMR), according to the new classification, labelling and packaging of chemical substances and mixtures, the so-called CLP Regulation classified CMR category 1a or 1b; or persistent, bioaccumulative and toxic (PBT), or very persistent and very accumulative (vPvB), or identified, on a case-by-case basis, from scientific evidence as causing probable serious effects to human health or environment of an equivalent level of concern as those above (e.g. endocrine disrupters). The substances SVHC are inserted in the Candidate list, and their number is 138. The consumer and downstream users of the products which contain substances SVHC must be informed of their presence and industry must be prepared to find alternatives because it is very likely that there will be some restrictions in their use in a near future. In fact, these substances can be transferred to the Authorization list, in order to be eliminated from the market or used after a date to be set (the so-called "sunset date") unless the company is granted by an authorization. Arsenic compounds in the Candidate list are: arsenic acid, diarsenic trioxide, trilead diarsenate, diarsenic pentaoxide, calcium arsenate, triethyl arsenate and hydrogen lead arsenate. All of them are carcinogenic cat. 1a. At present, in the Authorization list are present only diarsenic trioxide and diarsenic pentoxide with sunset date 05/21/2015, while arsenic acid has been proposed to be inserted in this list by 2013.

Arsenic compounds in the Candidate list

The uses of all these arsenic compounds present in the Candidate list will be reported in this note. The use of arsenic as wood preservative in Europe is forbidden but is still used in some countries, while it is used in Europe in some electronic and special glass applications. In Europe there is a consortium of 7 industries interested in the registration of arsenic compounds for Reach regulations, whose headquarter is in Berlin at Wirtschaftsvereinigung metalle. The Consortium consists of a number of EU and international companies showing interest in joint activities regarding the registration of the following compounds of arsenic under Reach: arsenic metal, tricalcium diarsenate, diarsenic trioxide, gallium arsenide, tricopper arsenide, trilead diarsenate and possible arsenic chloride.

Arsenic acid

Arsenic acid (H_3AsO_4) is used as fining agent in the manufacture [10] of speciality glass for removing bubbles from the glass melt. The addition of arsenic acid releases oxygen late in the fining process which makes bubbles more easily absorbed by the melt. Arsenic acid is used for domestic glass but also in the industrial special glass interchangeably with As_2O_3. A minor use (in the range of grams per year) appears to be as analytical standard in laboratories. It is used also for the fabrication of double and multi-layer printed circuit boards for electronic devices, telecommunication equipment and consumer appliances in the form of elemental arsenic (As) on the surface of the copper foil. Arsenic from arsenic acid is present in the final article (not arsenic acid itself), mostly in concentration <0.1%. Release of arsenic from the article is considered insignificant as the surface of the circuit boards is lacquered.

Arsenic acid is imported in Europe from 100 to 1,000 t/y, no production sites are present in Europe. Arsenic acid is used as processing agent but not as an intermediate. Arsenic acid is still widely used as a biocide for wood preservatives in countries outside EU, and some import with treated wood may take place. About 97% of the total ton-

nage is used as fining agent in the manufacture of speciality glass for removing bubbles from the glass melt. Due to concerns over the use of arsenic compounds, there are various other established alternative substances including: sodium sulphate (used in lead crystal), antimony trioxide (used in lead crystal), sodium/potassium nitrates with antimony trioxides (used in special glasses) and cerium oxide.

Tricalcium diarsenate

Tricalcium diarsenate ($Ca_3As_2O_8$) is generated in various metallurgical processes [11] in amount of 100-1,000 t/y in Europe from smelting and refining of nonferrous metals. By the decreasing of the use of arsenic compounds in the world, the amount of calcium arsenate disposed of as waste would probably increase. The main use of tricalcium diarsenate is in the manufacturing of diarsenic trioxide (As_2O_3) and in lesser amount as precipitating agent in copper smelting, and is not used in consumer products, but the higher amount is disposed as waste.

Trilead diarsenate

Trilead diarsenate ($Pb_3As_2O_8$) is imported in Europe [12] in an amount of 10-100 t/y and its main uses are as intermediate in the production of diarsenic trioxide obtained from smelting and refining of nonferrous metals used for manufacture of copper, lead and a range of precious metals.

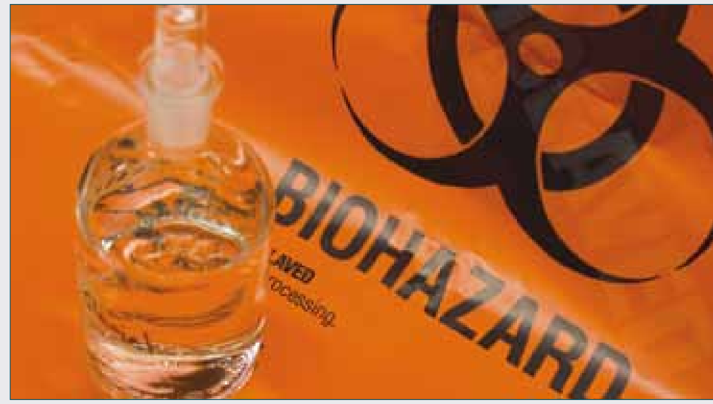
Trilead diarsenate is not used by downstream users or present in any consumer products. The trilead diarsenate is imported in complex by-products from smelting and refining of nonferrous metals. A substitution of diarsenic trioxide would result in a larger part of the arsenic in the trilead diarsenate ending up in waste from the metal recovery processes.

Lead hydrogen arsenate

Lead hydrogen arsenate ($PbHAsO_4$) was used in the past [13] as insecticide, wood preservative, plant growth regulator and rodenticide and prepared from

$$Pb(NO_3)_2(aq) + H_3AsO_4(aq) \rightarrow PbHAsO_4(s) + 2HNO_3(aq)$$

SICUREZZA



It is unlikely that there is any production of this compound within the EU and in US. No manufacture or import of lead hydrogen arsenate has been identified in the EU.

Triethylarsenate

Triethylarsenate [$CH_3CH_2O)_3AsO$] [14] is used as wood preservative and may potentially be used in the fabrication of integrated circuits (there is no production of triethyl arsenate within the EU). Only very small quantities (less than 100 kg per year) of triethyl arsenate has been developed for use in specialised doping applications for semiconductors. Use of triethyl arsenate as intermediate in electronic (semi-conductor) applications is exempt from authorisation.

Trilead diarsenate

Trilead diarsenate($Pb_3As_2O_8$) is present [15] in complex raw materials from smelting and refining of nonferrous metals used for manufacture of copper, lead and a range of precious metals. The raw materials are to some extent imported from countries outside EU. Registered quantities of trilead diarsenate manufactured are in the range of 10-100 t/y. According to the Arsenic Consortium the decreasing markets and use of arsenic compounds over the last decades let most copper and lead producers decide to eliminate the arsenic impurity from byproducts through the disposal of the waste trilead diarsenate be considered an intermediate in the production of diarsenic trioxide. Trilead diarsenate is imported in complex byproducts from smelting and refining of nonferrous metals. A part of the arsenic in the trilead diarsenate ultimately ends up in diarsenic trioxide. Trilead diarsenate is not used by downstream users or present in any consumer products. A substitution of diarsenic trioxide would result in a larger part of the arsenic in the trilead diarsenate ending up in waste from the metal recovery process. Large quantities of other arsenic compounds, generated as byproducts from metallurgical processes, are today disposed off as waste. Diarsenic trioxide may be manufactured without the use of trilead diarsenate as raw material.

Arsenic compounds in Authorization list

Diarsenic trioxide (As_2O_3) is the major source of arsenic [16] and is obtained to some extent as a byproduct of smelting and refining of copper, lead, cobalt, and gold ores, but mostly from copper production and in a smaller quantity from lead production. In Europe its use as a wood preservative is forbidden but it is still used in some countries. Arsenic oxide is produced in Europe in an amount of 1,820 t/y, 600 t/y are imported, 200 t/y are sent as waste and therefore about 2,200 t/y are used, about 700 t/y are consumed in Europe. The main uses of diarsenic trioxide seem to be in the manufacture of zinc by electrolysis and in glass production. In a lesser extent for manufacturing other chemicals and ultra-pure arsenic metal. In electrolysis applications As_2O_3 is added to zinc solution to precipitate metal impurities such as copper, cobalt, nickel and iron from solutions. Uses of arsenic for producing alloys are actually all based on arsenic metal. It is also used as a cytostatic in the treatment of refractory promyelocytic (M3) subtype of acute myeloid leukemia to treat it in patients who have not responded to other medications. It is also used as decolorizing agent for glass and enamels as refining and oxidizing agent for manufacturing special glass and lead crystal formulations. Elemental arsenic can be prepared by the reduction of diarsenic trioxide with charcoal.

Applications of arsenic metal in EU in the field of electronic is for (a) production of ultrapure gallium arsenide, (b) arsenic as a dopant, and (c) selenium based alloys. In all these applications diarsenic trioxide is claimed to be used under "strictly controlled conditions". About 150 t/y of As_2O_3 are used in the glass sector. In Italy it is used in Murano site, where about 80 manufactories, with about 800-1,000 workers, manufacture arsenic-containing art glasses. In this district the annual consumption of As_2O_3 is 8.2 t.

Diarsenic pentoxide [17] is estimated to be used in volume less than 210 t/y and can be synthesised by reacting diarsenic trioxide with oxygen under pressure or with oxidising agents, such as ozone, hydrogen peroxide and nitric acid or by dehydration of crystalline arsenic acid. Historically, diarsenic pentaoxide was used in the production of chromated copper arsenate (CCA), a wood preservative. This use is now banned in Europe although one site still formulates CCA (for export) in amount of 100 t/y and there may be articles (with 'old' CCA treated wood) still being imported and/or reused. CCA is prepared from copper oxide or sulphate, chromium oxide or sodium chromate and diarsenic pentaoxide. It is used in dying industry, in metallurgy (to harden copper, lead or gold in alloys), for manufacturing special glass and in wood preservation.

Conclusions

In the past we concentrated our attention mainly on the emission from chemical plants. Recent research indicates that hazardous chemicals can volatilize from consumer products during daily use, either directly to the air or in the form of contaminated dusts.

We can find contaminations from dresses, furniture, buildings, tools, instruments and products we use every day. These are called secondary pollutants.

We need research in the following directions:

1) stages of obtainment of safety data;
2) development of alternative screening to animal tests;
3) development of new processes and safer products.
4) improved flow of information down the supply chain;
5) sharing of knowledge and data on chemicals;
6) improved consumer confidence in chemicals;
7) stimulation of the industry for innovation.

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