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Sampling of chemical products for industrial use — Safety in sampling

Échantillonnage des produits chimiques à usage industriel — Sécurité dans l'échantillonnage

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FOREWORD

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Sampling of chemical products for industrial use — Safety in sampling

0 INTRODUCTION

In some cases the act of taking a sample exposes the sampler to a risk of personal injury or may risk the creation of hazardous conditions endangering the safety of others. This International Standard is intended to assist those engaged in sampling or in directing the activities of samplers, and also those responsible for premises within which a sampling operation is performed, to ensure that sampling shall be a safe operation.

Attention is also directed to the existence of legislation regulating the carriage of dangerous goods, and users of this International Standard should ensure compliance with these requirements and with those imposed by the carriers.

1 SCOPE AND FIELD OF APPLICATION

This International Standard gives recommendations relating to safety in the sampling of chemical products for industrial use.

2 GENERAL RECOMMENDATIONS

2.1 The following recommendations apply to all sampling operations whatever the nature of the material being sampled. The operator should have:

- safe access to and from the place where the sample is taken, and
- a safe working place with adequate light and ventilation.

Sampling points in fixed installations should be arranged to satisfy these needs as well as any special conditions arising from the nature of the material being sampled. Precautions shall be taken against falls when the sample is withdrawn from the top of a tank or tank vehicle and against the collapse of stacked containers or solids in bulk.

2.2 If the material being sampled is itself hazardous, the following general recommendations apply:

2.2.1 The sampling operation shall be carried out in such a manner as not to prejudice the security of the bulk.

This applies particularly to the sampling of fluids through cocks where the seizure of the cock in an open position could lead to the escape of large quantities of the fluid. It is recommended that the devices used for such sampling be

arranged so as to limit the total quantity drawn at any one time and to restrict the rate of flow to a convenient value.

In the case of liquids, it is reasonable to assume that spillages will occur and to provide both a drained trough and a tundish to trap spilt liquids safely and a permanent splash guard to protect the sampler.

For liquids and gases, provision shall be made whenever possible for isolating the sample point from the bulk or line by a valve near to, but not immediately adjacent to, the sample point so that in the event of an accident the flow may be controlled from a safe place.

In all cases it is part of the sampler's task to ensure satisfactory re-closure by appropriate personnel of all opened packages and sample points.

2.2.2 When it is necessary to purge or rinse a sample container with the material to be sampled, and this material presents a hazard, then appropriate facilities shall be provided for the disposal of material used in purging. Gases should be vented away from the vicinity of the sampler and other personnel.

2.2.3 The size of the sample and the frequency of sampling shall not be greater than are necessary for the examination proposed.

2.2.4 The sample in its container shall be carried in a suitable carrier designed and constructed to facilitate handling and to minimize the risk and consequences of breakage of the sample container.

2.2.5 The equipment, including all tools and containers, shall be compatible with the material being sampled and suitable for the intended purpose. For example, the sample container shall be capable of tight closure and shall be fitted with a pressure release. Samples shall be kept away from other chemical products liable to interact with them.

2.2.6 Before sampling, or as soon as possible, mark the container to indicate the nature of the material and the risks associated with it.

2.2.7 The person taking the sample shall be made fully aware of the nature of the hazards involved and the precautions to be taken. He shall be instructed in the use of all appliances provided for his safety, including fire extinguishers, protective goggles and clothing, etc. He shall

be instructed to report to an appropriate supervisor before and after taking the sample and shall report, preferably to the same authority, any unusual happening or situation.

If toxic substances are being sampled, he shall be instructed that, in the event of feeling unwell, he should report immediately to his supervisor.

2.2.8 The sampler should be accompanied by a second person whose task is to ensure the safety of the sampler. During the sampling operation this observer shall remain well clear of the sampling point and observe the whole operation. He shall be given specific instructions as to the action he shall take in an emergency and such instructions should always require that he first raises an alarm and does not attempt a single-handed rescue, except in extreme circumstances.

2.2.9 These general recommendations and the specific ones which follow should be used as a guide to the precautions necessary in preparing all samples.

2.2.10 Eye protection equipment should be used continuously wherever there is contact with chemicals.

2.2.11 It is stressed that those directing the activities of samplers shall consider in detail the consequences of minor mishaps which may occur, such as spillage, failure of cocks, etc. The sampler shall be given specific instructions covering both the normal situation and what he must do in the event of mishaps. Equally important are the specific instructions to be given to the safety observer present when toxic or dangerously corrosive materials are sampled (see 3.4 and 3.5).

3 SPECIFIC RECOMMENDATIONS FOR HAZARDOUS MATERIALS

The physical or chemical properties of the material being handled may be such that they can have a direct physiological effect or be such that, for example, fire or explosion risks are present. The degree of risk is extremely variable and only general guidance is possible. A general classification of risks is listed below together with the appropriate precautions which are additional to those given in 2.2. It should be assumed, in the absence of specific information to the contrary, that all new material being sampled is hazardous.

Many materials present more than one hazard; for example benzene is toxic and flammable and its vapour forms an explosive mixture with air.

Further information on individual substances is given in the following publications :

— *Substances chimiques dangereuses et proposition concernant leur étiquetage*. Conseil de l'Europe (Sous-comité de la santé et sécurité industrielle) — (Section chimie), Strasbourg, 3^{ème} édition 1971.

— *Dangerous properties of industrial materials*, by N. Irving Sax, Published by Reinhold.

— *Toxicity and metabolism of industrial solvents*, by Ethel Browning. Published by Elsevier.

— *Hazards in the chemical laboratory*, Ed. by G. D. Muir. Published by Royal Institute of Chemistry.

— *The care, handling and disposal of dangerous chemicals*, by P. J. Gaston. Published by The Institute of Science Technology.

In addition, the Manufacturing Chemists Association Inc. of Washington, D.C., U.S.A., publishes Chemical Safety Data Sheets relating to specific chemicals, and most manufacturers of chemicals are willing to advise prospective users and others on the handling of their products.

The following types of hazard may be encountered :

- explosive substances, including unstable substances not used as explosives (see 3.1);
- oxidizing substances (see 3.2);
- flammable substances (see 3.3);
- toxic substances (see 3.4);
- corrosive substances and irritants (see 3.5);
- substances dangerous by virtue of their physical state, notably their pressure and temperature (see 3.6);
- radioactive materials (see 3.7).

3.1 Explosive and unstable substances

3.1.1 Examples

Unstable substances kept under water or other liquids, concentrated hydrogen peroxide, ketone peroxides, peroxy organic acids, acetylene, etc.

3.1.2 Additional precautions

3.1.2.1 The sample container shall be closed so as to prevent loss of contents or evaporation, but the closure should provide for safe release of pressure.

3.1.2.2 The samples shall be protected from heat and shock and shall be transported only in a carrier designed to retain the sample in the event of a breakage or a leakage.

3.1.2.3 All spillages shall be reported for immediate action.

3.1.2.4 Naked lights, smoking and equipment which can produce sparks shall be prohibited.

3.1.2.5 Protective goggles and protective clothing should be worn.

3.1.2.6 The location of alarm systems and fire fighting equipment should be known.

3.2 Oxidizing substances

3.2.1 Examples

Liquid air and oxygen, oxidizing acids and their salts, hydrogen peroxide, etc.

The risk varies according to the nature of the substance and any combustible material with which it may come into contact, and also their degrees of subdivision. It is important to remember that the sampler's clothing is almost certainly combustible.

3.2.2 Additional precautions

3.2.2.1 The vicinity of the sampling operation shall be free of combustible matter as far as possible.

3.2.2.2 Adequate and appropriate fire extinguishers shall be available.

3.2.2.3 Sample carriers should not include combustible padding material.

3.2.2.4 Naked lights and smoking shall be prohibited.

3.2.2.5 All spillages shall be reported and corrected as soon as possible.

3.2.2.6 Protective goggles and protective clothing should be worn.

3.3 Flammable substances

3.3.1 Examples

In addition to flammable gases, liquids and solids (typified by hydrogen, fuel oil and coal), these include substances which, although not normally regarded as being flammable themselves, give combustible products if exposed to moisture (the alkali metal hydrides and calcium carbide are examples) and substances which ignite spontaneously in contact with air, for example white phosphorus, pyrophoric metals, etc.

The risk varies with the substance, its temperature and its state of subdivision. It is generally higher with liquids than with solids and is always high if the substance is volatile and yields flammable gases or is in a form which is readily dispersed in air. Attention is particularly directed to the risks of explosion which are present in enclosed spaces, where volatile fractions of the material including residual traces of solvents may accumulate, and in places where dust arising from combustible matter such as flour, starch, coal will, if dispersed, yield an explosive mixture. Those responsible for the sampling shall be acquainted with the flash and auto-ignition points of these substances, and the explosive concentrations limits of their vapours in air.

3.3.2 Additional precautions according to severity of risk

3.3.2.1 The vicinity of the sampling operation shall be free of possible means or aids to ignition. Naked lights, smoking and equipment which can produce sparks shall be prohibited.

3.3.2.2 Precautions shall be taken to ensure that static electrical charges cannot exist. Rubber-tyred vehicles shall be earthed before operations commence. In fixed installations, sampling points shall be individually earthed. It should be noted that, although these precautions will ensure the absence of a charge on the material being sampled, there is some possibility of the sampler or his clothing carrying a charge. Nylon overalls are often heavily charged in dry weather and cotton is preferred. The sampler should wear conductive foot-wear. The flow of fluids can generate static electricity, as can also the mixing of liquids, and sufficient time should be allowed to elapse after movement has stopped and before sampling is undertaken to ensure leakage to earth of the charge generated by movement.

3.3.2.3 Adequate and appropriate fire extinguishers shall be available.

3.3.2.4 All spillages should be reported and corrected as soon as possible. Spilt flammable liquids should not be allowed to enter drains unless they are water miscible and can be flushed away with a continuous flow of water.

3.3.2.5 Protective goggles and protective clothing shall be worn. Such clothing shall not in itself be flammable. Clothing made from synthetic fibres or plastics should not be worn.

3.3.2.6 Spontaneously flammable substances shall be handled either under an inert liquid or in an inert atmosphere.

3.4 Toxic substances

3.4.1 Introduction

Poisons may be assimilated by :

- ingestion (see 3.4.2);
- respiration (see 3.4.3);
- absorption (see 3.4.4).

In acute poisoning, i.e. from a single heavy dose, the effects may be associated with immediate discomfort and other symptoms, but in some cases there are delayed effects not appearing for some hours. In all cases, medical attention should be obtained.

Repeated low level doses of some substances are a health hazard because of accumulation of the poison itself in the body or by virtue of accumulated minor physiological changes. Persons exposed to this kind of risk should be periodically examined by a doctor.

Whenever toxic substances are handled or sampled, those persons exposed to the risk shall be made aware of the risk, the symptoms of poisoning and the nature of any delayed effects and be instructed to seek immediate medical assistance in the event of their feeling unwell in any way. Whenever the substance sampled may have a delayed effect, the sampler should be given a dated card stating that he has handled the named substance and bearing the name and telephone number of a medical officer able to advise on the subject.

Whenever personnel are sent away for medical attention, full details of the toxic hazard to which they have been exposed should be sent with them.

3.4.2 *Substances poisonous if ingested*

3.4.2.1 GENERAL

Under this heading are included solids and liquids of low vapour pressure, since poisonous substances of appreciable vapour pressure should be regarded as presenting a major risk via the respiratory system. If the solid is so finely divided that airborne dust may arise, then the risk should also be treated as for respiratory poisons (see 3.4.3).

3.4.2.2 ADDITIONAL PRECAUTIONS ACCORDING TO SEVERITY OF RISK

3.4.2.2.1 Smoking, the use of snuff, and eating or drinking in the vicinity of the poisonous substance should be prohibited.

3.4.2.2.2 Adequate washing facilities shall be provided and shall be used by the sampler after securing his sample containers and before leaving the site. Suitable facilities shall also be provided for adequate cleaning of all equipment after the samples are taken.

3.4.2.2.3 Sampling cocks for liquids should be arranged so that splashing cannot occur and so that any spillage is contained. Facilities shall be provided for isolating the sample point from the system by a valve near to, but not immediately adjacent to, the sample point.

3.4.2.2.4 All sample containers and tools should be clean and fit for use without rinsing with the product. Should rinsing be necessary, or a sample line require initial purging, suitable marked containers shall be provided for the surplus liquid and specific instructions issued directing the disposal of this surplus.

3.4.2.2.5 All spillages shall be reported immediately. If necessary, the sampler should wear suitable overalls so that, in the event of them being contaminated, they may be changed. Contaminated clothing should not be sent to a laundry or cleaners until a competent person, aware of the hazards involved, has taken the appropriate steps to remove the contamination.

3.4.3 *Respiratory poisons*

3.4.3.1 GENERAL

These include gases and volatile liquids and other poisonous liquids and solids which are being handled in such a way that airborne sprays or dusts may arise.

It is to be noted that, in one sense, all gases other than oxygen should be regarded as presenting a health hazard in that very high concentrations will lower the oxygen content of the atmosphere being breathed. Even nitrogen, although forming the major part of the air one normally breathes, is potentially fatal in this sense. It follows that it is generally desirable that the area in which gases of any description under pressure are sampled should be well ventilated.

When respiratory poisons present a health hazard, personnel protection may be afforded either by providing a supply of fresh air to a suitable face mask or by providing a gas mask fitted with a canister containing the appropriate absorbent. For some gases, notably carbon monoxide, and whenever heavy concentrations may occur, only a supply of fresh air to a sound face mask can be considered adequate. Absorbent canister protection should be used only if concentrations are low or if the substance is relatively involatile and the absorbent is primarily acting as a filter for dust and droplet particles.

On the other hand, the use of absorbent canisters is prohibited when the nature of the gas is such that the sampler will be incapable of detecting failure of the mask. Some individuals are virtually unable to detect the odour of hydrogen cyanide and awareness of hydrogen sulphide rapidly diminishes on continued exposure.

3.4.3.2 ADDITIONAL PRECAUTIONS

3.4.3.2.1 The appropriate respiratory protection shall be provided for and used by all persons engaged in the operation.

3.4.3.2.2 The sampler should be accompanied by a second person whose task is to ensure the safety of the sampler. During the sampling operation this observer shall remain well clear of the sampling point and observe the whole operation. He shall be given specific instructions as to the action he shall take in an emergency and such instructions should always require that he first raises an alarm and does not attempt a single-handed rescue, except in extreme circumstances.

3.4.3.2.3 Sampling cocks for liquids should be arranged so that splashing cannot occur and spillages are contained. Facilities shall be provided for isolating the sample point from the system by a valve near to, but not immediately adjacent to, the sample point.

3.4.3.2.4 Sample containers shall be hermetically sealed before leaving the site.

3.4.3.2.5 All spillages shall be reported immediately. If necessary, the sampler should wear suitable overalls so that, in the event of them being contaminated, they may be changed. Contaminated clothing should not be sent to a laundry or cleaners until a competent person, aware of the hazards involved, has taken the appropriate steps to remove the contamination.

3.4.4 Contact poisons

3.4.4.1 GENERAL

Contact poisons which enter the system through the skin are to be distinguished from corrosive substances covered by the next section (3.5). In general, corrosive substances are those which cause immediate damage to the tissues they contact and are noxious solely because of this damage. Contact poisons, on the other hand, are often absorbed through the skin into subcutaneous tissues without necessarily causing immediate surface damage or sensation. A few substances, for example hydrofluoric acid are both corrosive and, in this sense, contact poisons, but in general the contact poisons are more dangerous than corrosive substances as entry into the system is not immediately apparent to the victim.

The vapours of substances in this category should be assumed to be able to enter the body via the skin as readily as the liquid or solid itself and to be respiratory poisons. All these substances are poisonous if ingested.

It is recommended that skin contact with any organic liquids should be avoided and that, regardless of the nature of the chemicals being handled, a sampler should wash his hands free from contamination.

3.4.4.2 ADDITIONAL PRECAUTIONS

3.4.4.2.1 The appropriate protective clothing, etc. should be provided and worn. According to the severity of the risk this will be :

- full protective impervious outer clothing, including gloves and boots or overboots and a respirator; or
- impervious apron, gloves, boots and respirator or face mask; or
- face mask and gloves.

Attention is directed to the risk of unsuitable footwear acting as a trap for splashes and of unsuitable gloves absorbing and retaining chemicals.

3.4.4.2.2 Adequate washing facilities shall be provided, including a warm water shower for preference or a cold water shower. Before sampling, the sampler should test that the shower is in working order.

3.4.4.2.3 Contaminated clothing should be immediately removed.

3.4.4.2.4 The sampler should be accompanied by a second person whose task is to ensure the safety of the sampler. During the sampling operation this observer shall remain

well clear of the sampling point and observe the whole operation. He shall be given specific instructions as to the action he shall take in an emergency and such instructions should always require that he first raises an alarm and does **not** attempt a single-handed rescue, except in extreme circumstances.

3.4.4.2.5 Sampling cocks for liquids should be arranged so that splashing cannot occur and any spillage is contained. Facilities shall be provided for isolating the sample point from the system by a valve near to, but not immediately adjacent to, the sample point.

3.4.4.2.6 All sample containers and tools should be clean and fit for use without rinsing with the product. Should rinsing be necessary, or a sample line require initial purging, suitable marked containers shall be provided for the surplus liquid and formal instructions issued directing the disposal of this surplus.

3.5 Corrosive substances and irritants

3.5.1 GENERAL

The risks involved under this heading include the well known rapid effects of strong acids and alkalis, but attention is directed to the general undesirability of unnecessary exposure of the skin to any chemical. Comparatively harmless substances such as sodium carbonate can cause dermatitis; others may cause sensitization. The precautions to be taken are similar to those advised for contact poisons, but particular emphasis is placed on the use of safety goggles for eye protection. The corrosive action of strong acids and alkalis is such that immediate action to dilute them is absolutely essential and it is imperative that a drench shower or a plunge bath be available at the sampling point. These facilities should be protected against frost and shall be shown to be in working order before commencing sampling.

Additional precautions, as appropriate, should be taken as described in 3.4.3.2.

3.6 Substances dangerous by virtue of their physical state

3.6.1 GENERAL

These include substances at extreme temperatures and high pressures. In general, extremely cold and hot substances present similar hazards to those of corrosive substances, except that damage is virtually instantaneous and drench showers are of no value.

3.6.2 Additional precautions for substances dangerous by virtue of temperature

3.6.2.1 Eye protection against splashes is essential.

3.6.2.2 For very hot substances, shielding of the face and neck against radiant heat is necessary and protection of the eyes against radiation.