



THE SAFE PREPARATION OF GAS MIXTURES

Doc 39/22

Revision of Doc 39/14

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL

AVENUE DE L'ASTRONOMIE 30 • B – 1210 BRUSSELS

Tel: +32 2 217 70 98

E-mail: info@eiga.eu • Internet: www.eiga.eu

 **Documents**
Document Sharing Hub



THE SAFE PREPARATION OF GAS MIXTURES

Disclaimer

All technical publications of EIGA or under EIGA's name, including Codes of practice, Safety procedures and any other technical information contained in such publications were obtained from sources believed to be reliable and are based on technical information and experience currently available from members of EIGA and others at the date of their issuance.

While EIGA recommends reference to or use of its publications by its members, such reference to or use of EIGA's publications by its members or third parties are purely voluntary and not binding.

Therefore, EIGA or its members make no guarantee of the results and assume no liability or responsibility in connection with the reference to or use of information or suggestions contained in EIGA's publications.

EIGA has no control whatsoever as regards, performance or non performance, misinterpretation, proper or improper use of any information or suggestions contained in EIGA's publications by any person or entity (including EIGA members) and EIGA expressly disclaims any liability in connection thereto.

EIGA's publications are subject to periodic review and users are cautioned to obtain the latest edition.

© EIGA grants permission to reproduce this publication provided the Association is acknowledged as the source

Table of Contents

1	Introduction	1
2	Scope and Purpose	1
3	Definitions	1
3.1	Publications terminology	1
3.2	Technical definitions	1
4	Principles of safe gas mixing	3
4.1	Principle 1: Written instructions shall be provided	3
4.2	Principle 2: Equipment and facilities shall be properly designed	3
4.3	Principle 3: Written instructions shall be prepared by competent staff using recognised data	3
4.4	Principle 4: Personnel shall be trained	3
4.5	Principle 5: Intended cylinder-content shall be identified before filling	4
4.6	Principle 6: Supply gases and cylinders shall be controlled	4
4.7	Principle 7: Facilities and procedures shall be audited	4
5	Feasibility and classification of gas mixtures	4
5.1	Gas mixture availability constraints	4
5.2	Gas mixture categories	4
6	Gas mixing instructions	5
6.1	General controls	5
6.2	Mixture-specific manufacturing instructions	5
6.3	Personnel responsible for preparing & authorising gas mixing instructions	5
6.4	Safety system	5
6.5	Approval of gas mixing instructions	6
6.6	Adjustment of gas mixing instructions	6
6.7	Adjustment of existing mixtures	6
6.8	Consideration of mixing methods	6
6.9	Compatibility considerations	7
6.10	Identification and labelling	9
7	Design and operation of gas mixing facilities	9
7.1	General requirements	9
7.2	Specific requirements	10
8	Personnel training	14
8.1	All personnel	14
8.2	Cylinder reception personnel	15
8.3	Gas disposal personnel	15
8.4	Cylinder maintenance personnel	15
8.5	Cylinder filling personnel	15
8.6	Gas analysis personnel	16
8.7	Cylinder shipping personnel	16
8.8	Plant maintenance personnel	16
8.9	Personnel engaged in preparing operating procedures and gas mixing instructions	17
8.10	Personnel engaged in plant and equipment design	17
8.11	Other personnel	18
8.12	First-aid training	18
9	Safety	18
9.1	Provision of personal protective equipment <u>and tools</u>	18
9.2	Safety rules	18
9.3	Emergency planning	18
9.4	Audits	19
10	References	21
11	Additional References	22
	<u>Appendix A – List of unstable gases (Informative)</u>	24

1 Introduction

For many years, the gas industry has produced a wide range of gas mixtures. All gas mixing operations require the normal safety procedures, practices and controls that are followed when filling standard industrial gases. Additional controls are required when mixing potentially incompatible gases. For this reason, great care is necessary during the preparation of such mixtures to ensure that no uncontrolled reactions take place.

Regulations and procedures for gas mixing vary in some details from one manufacturer to another, however, they should always be based on the same safety principles. Details concerning the safe manufacture of oxidant-fuel mixtures are described in EIGA Doc 139, *Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders* [1].¹

Manufacturers of gas mixtures for medical use should also refer to EIGA Doc 99, *Good Manufacturing Practice Guide for Medicinal Gases* [2].

2 Scope and Purpose

The sole aim of this publication is to set out the basic requirements to ensure that gas mixtures are manufactured safely. This publication is not intended to be a manual on how to manufacture gas mixtures.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publications terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Cylinder

Any transportable receptacle that can be filled with gas under pressure.

¹ References are shown in bracketed numbers and are listed in order of appearance in the reference section

3.2.2 Filling ratio (Also known as filling degree or filling density)

Ratio of the mass of gas to the mass of water at 15 °C (59 °F) that would fill completely a pressure receptacle fitted ready for use, see ADR [3].

NOTE—In other jurisdictions, the filling ratio may be defined slightly differently.

The filling ratio (f) is expressed as the ratio: (M/C),

Where:

M = mass of gas filled (kg)

C = cylinder water capacity (L)

3.2.3 Hazop

Technique to identify and assess potential hazards that could arise during the operation of plant or equipment. A hazop study is carried out to assess the potential effects of various malfunctions of the equipment or plant (e.g., reverse flow, excessive temperature or pressure, etc.).

3.2.4 Hygroscopic

Substance that has an affinity for water. Many acid gases are hygroscopic (e.g., hydrogen chloride) and, when in the wet state, are normally much more reactive with materials of construction.

3.2.5 Liquefied gas

Gas which when packaged under pressure for carriage is partially liquid at temperatures above –50 °C (–58 °F).

A distinction is made between:

- High pressure liquefied gas—a gas with a critical temperature above –50 °C (–58 °F) and equal to or below 65 °C (149 °F); and
- Low pressure liquefied gas—a gas with a critical temperature above 65 °C (149 °F).

3.2.6 Intermediate analysis

Analysis carried out part-way through the process of filling a gas mixture into a cylinder (or cylinders). Such an analysis is normally carried out to confirm the concentrations (and sometimes the identities) of the components that have been filled before a subsequent component is added.

3.2.7 Passivation

Procedure that is applied where there is a possibility of a reaction between a reactive gas and the container or system into which it is going to be introduced. Passivation ensures that any reaction takes place under controlled conditions. Passivation may also be used to ensure the stability of a gas mixture. Passivation is usually carried out using a mixture containing the reactive gas diluted in an inert gas.

3.2.8 Premix

Gas mixture that is used as one of the supply gases during the filling of a gas mixture. The use of premixes can enable low concentration components to be filled accurately and can also eliminate any potential hazards when filling certain gas mixtures containing potentially incompatible components.

3.2.9 Written instructions

Work instructions that are printed out on a paper or available digitally on an electronic device such as personal computer or tablet.

4 Principles of safe gas mixing

This section sets out the basic principles that shall be followed to ensure gas mixtures are produced safely.

4.1 Principle 1: Written instructions shall be provided

Gas mixtures shall only be filled in accordance with written and approved instructions. Normally the instructions issued will comprise operating procedures for the plant and equipment and specific instructions for each gas mixture to be prepared.

4.2 Principle 2: Equipment and facilities shall be properly designed

Gas mixtures shall only be prepared in properly equipped and approved facilities where provisions have been made for:

- Pressure and material compatibility of filling equipment with the intended mixtures;
- Adequate segregation of filling flammable and oxidant gases and other potentially incompatible components to clearly defined areas;
- Prevention of feed-back of gas from filling systems into supply gas systems; and
- Safe and environmentally responsible disposal of waste gases. EIGA Doc 30, *Disposal of Gases* gives further detailed information [4].

4.3 Principle 3: Written instructions shall be prepared by competent staff using recognised data

Gas mixing instructions shall be prepared by trained and competent staff that check for:

- availability of recognised data;
- safety of the proposed method of manufacture and the final mixture;
- unsafe situations that could arise from the liquefaction (condensation) of components during and after mixing;
- quantity of product versus cylinder size (particularly with respect to liquefied gas mixtures, to ensure that the cylinder is not over-filled); and
- tolerance requirements for safe mixing.

4.4 Principle 4: Personnel shall be trained

Personnel engaged in gas mixing shall be given training based on written instructions covering:

- all aspects of preparing gas mixtures;
- key characteristics of the gases being handled and the safety requirements when dealing with them;
- recognition and mitigation of the hazards during mixture preparation that is found to be unsafe;

- protective clothing and equipment; and
- safety rules, emergency, and first-aid procedures.

The training shall be properly recorded, updated regularly, and competency assessed and confirmed.

4.5 Principle 5: Intended cylinder-content shall be identified before filling

Before any cylinder is filled, it shall be clearly identified with the names and respective nominal concentrations of the intended mixture components (or the mixture registered trade name where appropriate). Alternative methods of identification that give an equivalent level of safety may be used. The content and status of the container during the production process shall also be recorded.

4.6 Principle 6: Supply gases and cylinders shall be controlled

There shall be adequate controls to ensure that:

- only the intended gases are used to prepare gas mixtures; and
- cylinders are suitable for the mixture, properly prepared, and free of any contaminants that can affect the safety of the filling process and/or the intended use of the mixture.

4.7 Principle 7: Facilities and procedures shall be audited

All operational gas mixing facilities and procedures shall be audited regularly for compliance with the previous six principles, 4.1 to 4.6.

5 Feasibility and classification of gas mixtures

There are more than 100 commonly available liquefied and permanent gases and a large number of liquids whose vapours are used in the formulation of gas mixtures. Gas mixtures can contain any number of components at almost any concentration, provided they are safe and technically feasible to produce. Hence, the potential range of available gas mixtures is almost infinite. This section gives basic guidance on the types of gas mixtures produced and the constraints that may be applicable to their manufacture.

5.1 Gas mixture availability constraints

The main constraints on the availability of gas mixtures are concerned with:

- Safety—The gas industry will not manufacture any gas mixture that could compromise the integrity of the cylinder, valve, dip tube, or filling system; and
- Technical feasibility—The physical and chemical properties of some mixture components have a limiting effect on what can be practicably manufactured (e.g., a very low vapour pressure can limit the concentration of the component and the final filling pressure of the gas mixture).

5.2 Gas mixture categories

Generally, gas mixtures can be grouped into two broad categories:

- Standard gas mixtures—those that are filled repeatedly on a large scale. Normally these are relatively simple, containing a small number (typically two or three) common standard gas components with filling and analytical tolerances that are not critical; and
- Special mixtures—those that are filled on a smaller scale than standard gas mixtures. These mixtures are frequently more complex than standard gas mixtures.

6 Gas mixing instructions

Gases and vapours may be mixed in any combinations at any concentrations provided the mixture is technically feasible and safe, i.e., components are compatible with each other and with the cylinder and its valve, both during filling and after mixing. The purpose of this section is to set out the principles and controls necessary to ensure safe gas mixing instructions can be formulated and issued. Some additional guidance is given on possible gas mixture filling strategies.

6.1 General controls

Gas mixtures shall only be filled against written and approved procedures. Such procedures shall cover both the filling equipment to be used and the specific gas mixture to be prepared.

6.2 Mixture-specific manufacturing instructions

Instructions specific to the mixture to be filled shall include:

- details of the cylinder and valve and their preparation;
- components and quantities to be added and the sequence of addition;
- means and methods of measuring the components into the cylinder and the filling equipment to be used;
- any special constraints relating to the rate at which the components are to be added (e.g., to minimise temperature increases);
- method of mixing the components; and
- any intermediate analysis requirements (i.e., analysis to be carried out during the filling process to confirm the correct quantities of some components have been filled before the addition of other component[s]).

6.3 Personnel responsible for preparing & authorising gas mixing instructions

Such personnel shall have sufficient technical education and relevant experience to be able to fully understand the chemical, physical and engineering principles involved in the formulation of mixing instructions and their subsequent approval. There shall be a list of authorised personnel. Listed personnel should not be placed under undue production or commercial pressures whilst preparing and authorising gas mixing instructions. Such personnel shall work to formalised procedures and instructions and shall work and communicate closely with the personnel who design gas mixing facilities and who prepare gas mixtures.

6.4 Safety system

The safety system shall ensure that gases are not mixed without proper written and approved mixing instructions and that the integrity of both the filling system and the containers being filled are not compromised. The gas mixing instruction approval system shall take into account:

- Enquiry and quotation stage—to ensure that no commitment is given to prepare an unsafe mixture;
- Acceptance of order into processing system—to ensure that orders for unsafe mixtures are not accepted;
- Formulation of gas mixing instructions—to ensure that formulation is only undertaken by trained and authorised personnel;

- Approval of gas mixing instructions—to ensure approval of written instructions prior to issue to production (see 6.5); and
- Computer systems used to calculate and/or store gas mixing instructions—to ensure that non-approved instructions are not released for production use. Safeguards against keying errors shall be incorporated into the system.

6.5 Approval of gas mixing instructions

Gas mixing instructions may be formulated manually or with the aid of appropriate computer software and database(s). Such software and database(s) shall be validated as correct and secure. Once formulated, gas mixing instructions may be issued directly for use and/or may be stored in a computer file for subsequent issue. Where a computer file is used for the storage and issue of previously formulated gas mixing instructions, all entries into the file shall be checked to ensure there are no keying errors including checking units of component concentration and method of measurement during filling. There shall be no unauthorised modification of the file content.

Gas mixing instructions, whether formulated manually or with the aid of a computer shall be checked, before issue for use or entry into a computer file for subsequent use as follows:-

- All instructions—by at least one competent person (the blender can be the competent person); and
- Instructions for mixtures that contain potentially incompatible components—by at least one additional competent person. For compressed oxidant-fuel gas mixtures refer to EIGA Doc 139 [1].

6.6 Adjustment of gas mixing instructions

The adjustment of existing gas mixing instructions shall be subject to the same rigorous controls as new instructions. They shall not be adjusted without the authorisations detailed in 6.5.

6.7 Adjustment of existing mixtures

When a gas mixture is found to be out of tolerance after analysis, it is sometimes practicable to adjust the composition of the mixture by addition of one or more of the mixture component gases. Before this operation is undertaken, written instructions shall be formulated. Where the mixture adjustment involves addition of a gas that is potentially incompatible with the existing mixture components, the mixture adjustment instructions shall be reviewed according to 5.1 and approved by a competent person who is accountable for safety.

6.8 Consideration of mixing methods

The methods generally available for the preparation of gas mixtures in cylinders are listed in the following sections, together with the considerations necessary for safe operation. Combinations of two or more of these methods may sometimes be used.

These methods are also described in ISO standards, see Section 11.

6.8.1 Static methods

In this method, the mixture is produced directly in the cylinder by adding measured quantities of each of the mixture components. Mixing of these components may not be instantaneous and concentration gradients can be present during and immediately after filling the cylinder. This shall be taken into account to ensure that no dangerous mixtures can exist during filling. There are three commonly used methods of measuring the quantities of mixture components into the cylinder during filling. It may be appropriate to use a combination of these methods to prepare some gas mixtures. These static methods are as follows: