INTERNATIONAL STANDARD

ISO 14707

First edition
2000-08-15

Surface chemical analysis — Glow discharge optical emission spectrometry (GD-OES) — Introduction to use

Analyse chimique des surfaces — Spectrométrie d'émission optique à décharge luminescente — Introduction à son emploi

Reference number
ISO 14707:2000(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

© ISO 2000

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

Printed in Switzerland

Copyright International Organization for Standardization
Provided by IHS under license with ISO
No reproduction or networking permitted without license from IHS

Not for Resale

Contents

Page

Annex

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 14707 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

Annex A of this International Standard is for information only.

Introduction

Glow discharge optical emission spectrometry (GD-OES) is used to determine the elemental composition of solid samples. GD-OES may be used for either bulk or depth profile analysis. In bulk analysis, changes in elemental composition with depth into the specimen are assumed to be negligible. In contrast, the main goal of depth profile analysis is usually to gain information concerning such changes of composition. Layer thicknesses amenable to GD-OES depth profiling range from a few nanometres to approximately one hundred micrometres.

As is true for any instrumental analysis method, the quality of a GD-OES analysis depends markedly on the correct optimization and operation of the instrumentation. This document provides guidelines of practice that should be followed to ensure that GD-OES analyses are of the highest possible quality.

Surface chemical analysis — Glow discharge optical emission spectrometry (GD-OES) — Introduction to use

1 Scope

This International Standard provides guidelines that are applicable to bulk and depth profiling GD-OES analyses. The guidelines discussed herein are limited to the analysis of rigid solids, and do not cover the analysis of powders, gases or solutions. Combined with specific standard methods which will become available in the future, these guidelines should enable the regulation of instruments and the control of measuring conditions.

Although several types of glow discharge optical emission source have been developed over the years, the guidelines contained in this document use the Grimm type as an example. This is because the Grimm type device accounts for a very large majority of glow discharge optical emission devices currently in use. It should be clearly understood that the guidelines contained herein are equally applicable to other source designs, such as the Marcus type, and that the Grimm type device is used only as an example.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3497:1990, *Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods*.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*.

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*.

ISO 5725-4:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 4: Basic methods for the determination of the trueness of a standard measurement method*.

ISO 6955:1982, *Analytical spectroscopic methods — Flame emission, atomic absorption, and atomic fluorescence — Vocabulary*.

3 Terms and definitions

For the purposes of this International Standard, the terms and definitions given in ISO 3497, ISO 5725-1, ISO 5725-2, ISO 5725-3, ISO 5725-4 and ISO 6955 apply.

4 Principle

Analysis by GD-OES involves the following operations:

a) preparation of the sample to be analysed, generally in the form of a flat plate or disc of dimensions appropriate to the instrument or analytical requirement (round or rectangular samples with a width of 10 mm to 100 mm are suitable);

b) atomization and excitation of the analytes to be determined by means of ion sputtering and energy transfer processes occurring in the glow discharge;

c) measurement of the emission intensities of characteristic spectral lines of the analytes (for depth profiling, emission intensities are recorded as a function of time);

d) determination of the analyte concentrations contained in the sample by calibration with reference samples of known composition (for depth profiling, the sputtered depth as a function of time is also determined by calibration with reference samples of known composition and sputtering rates).

A diagram of a typical GD-OES system is presented in Figure 1. GD-OES is based on the use of a glow discharge device as an optical emission source. The glow discharge device consists of a vacuum chamber filled with an inert gas, usually argon. The glowing plasma, from which the discharge takes its name, is maintained by a controlled high voltage of 500 V to 1 000 V applied between the anode and cathode in the inert gas. The solid sample to be analysed serves as the cathode.

Atomization of sample material in the glow discharge is the result of ion sputtering. Inert gas ions formed in the plasma are accelerated toward the cathode surface by the electric field in the plasma. When an ion collides with the surface, its kinetic energy may be transferred to atoms on the surface, causing some of these surface atoms to be ejected into the plasma. Once in the plasma, these sputtered sample atoms may be excited through inelastic collisions with electrons or other species. The majority of these excited analyte atoms then emit characteristic optical emission upon relaxing into the lower electronic state. This optical emission is translated into an analytical signal by means of appropriate optical and electric components. A polychromator is commonly employed, so that many elements may be quantified simultaneously. Spectral lines that are not contained in the line set of the polychromator can be accessed by means of a scanning monochromator, if one is available. In practice almost all elements in the periodic table can be determined, including metals, metalloids and non-metals.

5 Apparatus

At a minimum, the apparatus consists of the following:

5.1 Glow discharge optical emission source

A diagram of a Grimm type glow discharge optical emission device is shown in Figure 2. Several modifications in the device have been introduced by instrument manufacturers, but the basic principle is not different from that shown in Figure 2. As noted in clause 4, the sample effectively serves as the cathode. The anode takes the form of a tube with an inner diameter of typically 2,5 mm to 8 mm. The distance between the front face of the anode and the surface of the cathode is usually between 0,1 mm and 0,3 mm. As a result, ion sputtering is confined to a circular region of the sample surface with a diameter approximately equal to the inner diameter of the anode.

The glow discharge device requires several peripheral pieces of equipment for its operation. These include an electric power supply, one or two vacuum pumps, a source of inert gas, a means of delivering that gas into the device in a controlled manner and a vacuum gauge. A cooling device, such as a metal block with circulating cooling liquid, is sometimes necessary for thin samples.

a) **Source parameters**

Glow discharge devices may be operated in either direct current (dc) or radio-frequency (rf) mode. Combinations of these two modes, such as the use of an rf voltage superposed onto a dc voltage, have also been reported.

1) For dc operation, the pertinent electrical parameters are discharge current (5 mA to 200 mA) and voltage (400 V to 2 000 V). In addition to the electrical parameters, other parameters are important for the character-

Key

1	Spectrometer
2	Vacuum chamber for UV spectra
3	Electrical lead-in
4	Preamplifier
5	Light intensity measuring circuit
6	Vacuum control system
7	Photomultiplier
8	Exit slit
9	Rowland circle
10	Cooling system
11	Gas control system
12	RF power supply
13	DC power supply
14	Control circuit
15	Local computer
16	Sample
17	Personal computer system
18	Grating
19	Entrance slit
20	Lens
21	Glow discharge source
22	Glow discharge control system

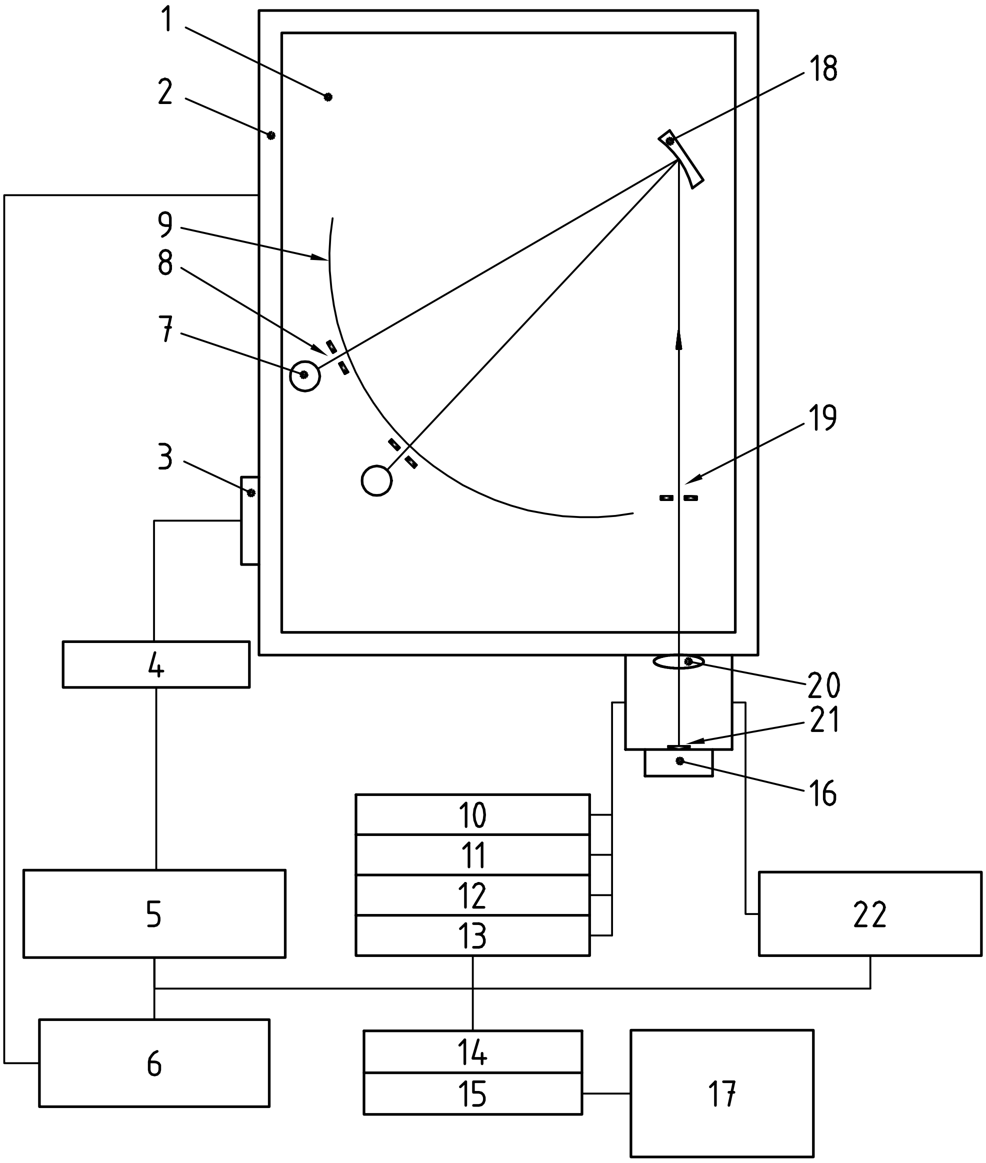


Figure 1 — Schematic diagram of a GD-OES system

istics of the device. These include the inner diameter of the anode (2,5 mm to 8 mm), gas type and purity (for example, argon, $>$ 99,999 %), gas flow rate (0,2 l/min to 0,3 l/min, see note below) and physical characteristics of the sample material (for example, secondary electron emission yield and sputtering yield). The combined effects of all of these factors determine the spectrochemical character of the glow discharge. Generally, it is recommended that the gas flow rate be varied in real time, in order to achieve constant voltage and current. As an example, typical operating conditions for dc GD-OES bulk analysis of low-alloy steels are 0,25 l/min argon flow rate, 600 V to 1 000 V discharge voltage and 30 mA to 60 mA discharge current, for an anode of 4 mm inner diameter.

NOTE It should be understood that the discharge gas flow rate is the practical means of controlling the source operating pressure, and so suggested ranges are very much source specific, and are provided here only with reference to the Grimm lamp example.

2) Typical conditions for rf glow discharge include the same range of argon flow rate and similar discharge power and voltage as in dc operation. In terms of the electrical parameters, it is important to note that GD-OES instruments usually measure either the incident power or the applied RMS voltage. In the former case, it must be understood that the incident power is the power delivered to the glow discharge system by

the rf power supply. Because of power losses in cables, the cooling system, etc., the effective power is generally lower than the incident power (i.e., the power actually dissipated within the glow discharge itself). Similarly, in the latter case, the measured voltage may not be an accurate representation of the effective discharge voltage. The rf power supply may be of either the fixed or the variable frequency type. In either case, the rf frequency is usually between 3 MHz and 41 MHz. Common fixed frequencies are 13,56 MHz, 27,12 MHz and 40,68 MHz.

In addition to conductive samples, rf GD-OES allows the analysis of non-conductive samples. For non-conductive samples, the rate at which ion sputtering erodes the sample surface is usually in the range of 50 nm/s to 150 nm/s. Non-conductive layers on conductive substrates may also be examined. For these samples, the applied rf voltage is generally higher than for conductive samples.

b) **Source/spectrometer interface**

The optical radiation emitted from excited sample atoms is guided by lenses or mirrors to the entrance slit of the spectrometer. If spectral lines with wavelengths below 200 nm (i.e., vacuum UV) must be used, the entire optical path from the glow discharge source to optical detector must be sufficiently free of molecular oxygen. This is because O_2 has very strong absorption bands below 200 nm. Oxygen can be eliminated from the optical system by flushing the system with a suitable pure gas such as nitrogen (or argon), or by evacuating the optical path to a pressure less than 0,01 Pa. The window separating the source and the spectrometer must be cleaned periodically.

5.2 Optical unit

The most common instruments are equipped with a simultaneous spectrometer (for example, a direct reader, or polychromator) with 20 to 50 fixed channels. It is also common to combine this with a sequential spectrometer (i.e., monochromator). With either simultaneous or sequential spectrometers, the spectral bandpass, and thus the effective spectral resolution, is determined by the dispersion of the instrument and the geometrical slit widths. If an array-type detector, such as a charge coupled device (CCD) or a charge injection device (CID), is used, special spectrometer configurations are necessary to cover the wide spectral range of the detector.

5.3 Photoelectric detectors and measuring devices

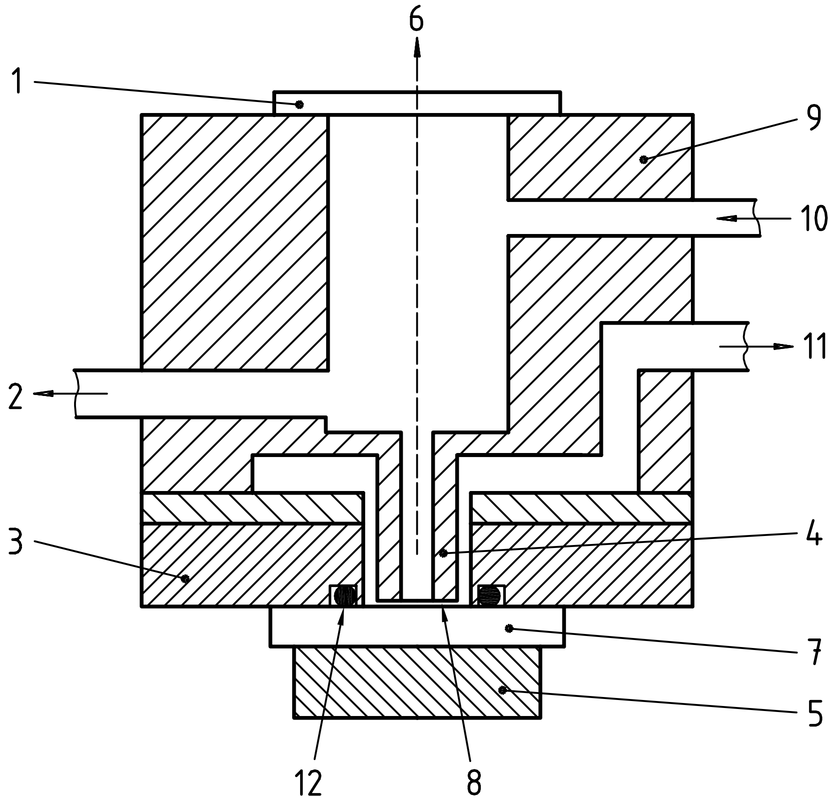
Most glow discharge spectrometers are equipped with photomultiplier tubes for signal detection. To achieve optimum performance (i.e., signal intensity, sensitivity and power of detection), photomultipliers with low dark current and maximum quantum efficiency are required. The photomultiplier gain shall be selected properly to avoid non-linear response and saturation. This is accomplished by measuring selected samples containing different analyte concentrations and adjusting the gain in such a way that sufficient sensitivity at the lowest analyte concentrations is ensured, without saturation of the detector at the highest analyte concentrations. The amplified detector output should be digitized by means of analog-to-digital converters and transferred to a computer for data storage and further evaluation.

6 Procedure

6.1 Verification tests

6.1.1 General

In order to obtain analytical data of the highest possible quality, it is necessary to verify the performance of the spectrometer and all devices connected to the system. If such verification was not performed by the instrument manufacturer at the time of installation, then it should be done by the user. Verification should be also performed periodically. The principal components to be checked are the glow discharge source, the optical unit and the electric measuring devices.



Key

1	Window
2	Vacuum line B
3	Cathode block
4	Interior wall of anode
5	Cooling block
6	To spectrometer
7	Specimen (cathode)
8	Front face of anode
9	Anode
10	Gas inlet
11	Vacuum line A
12	Gastight vacuum sealing (O-ring)

Figure 2 — An example of a glow discharge source (Grimm type)

6.1.2 Glow discharge source

The following should be examined using adequate source parameters [see 5.1a)] and a suitable sample (for example, iron):

a) the stability of sputtering and plasma composition while the discharge is running, using intensity ratios of spectral lines of interest to either the background continuum or to plasma gas lines;

b) the sputtering rate of the chosen sample at the selected discharge conditions;

c) the gas quality and tightness of the vacuum system, especially if elements that exist in the Earth's atmosphere are to be determined;

d) the condition of the anode (for example, the spacing between its front face and the sample surface).

6.1.3 Optical unit and electric measuring device

The following should be verified:

a) the alignment of the glow discharge emission source with respect to the optical axis of the spectrometer (i.e., the image of the source on the entrance slit);

b) the spectral resolution of the spectrometer and the accuracy and stability of the wavelength adjustment over the useful spectral range, using a suitable sample (for example, low-alloy steel);

c) the stability of the detector readout with the glow discharge on and off, measured over a suitable period of time.

6.2 Determination

6.2.1 General

In order to achieve the full analytical potential of GD-OES in terms of limit of detection, accuracy and reproducibility, the measurement shall be performed under suitable discharge conditions, which are determined for the particular sample groups to be analysed in accordance with the following instructions.

Quantitative analysis by GD-OES involves the following steps:

6.2.2 Preparation of the required calibration samples

The reliability of the calibration procedure largely determines the accuracy of the analytical results obtained. It is necessary to use sample materials of well-known composition (either reference materials or secondary standards) in optical emission spectrometric analysis. The calibrants should, to the largest possible extent, resemble the samples under measurement with respect to chemical composition and metallurgical pretreatment. The calibrants are used to determine the sputtering rate and emission intensity of analyte elements as a function of concentration.

Requirements for sample shape and size are determined by the design of the source. Normally, the sample shall be flat and large enough to cover the contact surface of the sealing medium for vacuum (for example, O-ring in Figure 2). Moreover, the surface of the sample shall be sufficiently smooth to form a suitably tight vacuum seal. In order to maintain a suitable discharge, sputtered sample material that is deposited onto the interior wall and front face of the anode shall be regularly removed by means of a cleaning device. A reamer is commonly employed for this purpose.

To resolve problems that may occur during measurement, the following points should be checked using suitable calibration samples:

a) the range of concentration for each element to be determined;

b) the presence or absence of interfering spectral lines of species associated with the sample or the discharge gas;

c) the contribution of the background emission and its temporal fluctuation;

d) adequate sputtering and data acquisition rates for depth profiling.

6.2.3 Optimization of measuring conditions

Usually, the operating instructions supplied by the instrument manufacturer state the operations to be carried out in setting up the instrument using calibration samples. The operations typically specified are as follows:

a) mount a test sample on the glow discharge device and produce an ultimate vacuum of the order of 0,1 Pa in the source;

b) set the appropriate conditions (for example, gas flow rate or pressure, voltage, current, power, frequency);

c) ignite the glow discharge;

d) select the wavelengths of the elements to be determined;

e) adjust the entrance slit or other specified optical components to optimize signal intensity, and evaluate the stability of the discharge [for the commonly used polychromator, this procedure is known as profiling the spectrometer or instrument (not to be confused with depth profiling)].

In the case of a non-linear calibration, line interference or self-absorption effects should be considered. If necessary, a different spectral line should be selected.

6.2.4 Quality check of results

The quality of the GD-OES results should be explicitly checked as follows:

a) One or more certified reference materials should be analysed as check standards. Analyte concentrations determined with GD-OES should agree with the certified concentrations within appropriate statistical bounds (see ISO 5725-1, ISO 5725-2, ISO 5725-3 and ISO 5725-4).

b) Whenever practical, analyte concentrations in selected unknown samples determined with GD-OES should be compared to the concentrations obtained by means of a second analytical method. Preferably, the second method should be one that is known to provide high-quality determinations for the analytes and matrices under measurement. In comparing the results from the two methods, particular attention should be given to their relative repeatability and reproducibility (see ISO 3497 and ISO 5725-1, ISO 5725-2, ISO 5725-3 and ISO 5725-4).

6.2.5 Test report

It is recommended that the following parameters, where applicable, be recorded and reported in conjunction with presentation of analytical results:

a) type of excitation (dc or rf);

b) for dc operation, discharge voltage and current;

c) for rf operation, forward and reflected incident power and frequency (if available also the effective power and rf voltage);

d) gas type and purity;

e) gas flow rate;

f) gas pressure (including type and location of pressure gauge);

g) anode shape and dimension (particularly the inner diameter);

h) measuring or sputtering time;

i) wavelengths of analytical lines;

j) analyte concentrations;

k) limits of detection;

l) repeatability of measurements;

m) sputtered mass and depth.

Annex A
(informative)

Safety

A.1 General

Although no official text has yet been published concerning the problems of safety in GD-OES, and although no generally recognized rules or recommendations relate specifically to this technique, a certain number of precautions should be taken to assure the safety of operators and their environment. These precautions relate to the following specific aspects:

a) the use of a high-voltage power supply and grounding of the instrument;

b) the use of radio frequencies;

c) the use and storage of compressed-gas cylinders;

d) safety checks before and during operation.

A.2 Use of a high-voltage power supply and grounding of the instrument

Electrical connections should comply with the regulations in force. Particular care should be taken to ensure that the connection of the instrument to ground is correct, and the efficiency of the ground connection should also be checked. The high voltage between samples and anode should be off when samples are being handled.

A.3 Use of radio frequencies

Lacking certain knowledge of harm caused by radio frequencies, all radiation should be as low as possible. The Electromagnetic Compatibility Directive (Directive 89/336/EEC) was adopted in May 1989, and came into force on 1 January, 1992. This applies to nearly all electrical and electronic equipment. It requires that equipment neither cause excessive electrical interference nor be unduly susceptible to it.

A.4 Use and storage of compressed-gas cylinders

The compressed-gas cylinders should regularly be tested by the appropriate authorities. Preferably, cylinders should never be stored or used inside the laboratory. Rather, they should be located at all times outside the laboratory in a place that is well ventilated, away from direct heat, and accessible only to service and safety personnel. The cylinders should be provided with suitable pressure-reducing valves. If more than one cylinder is to be used or stored in close proximity, it is advisable to indicate in some way which cylinder or cylinders are currently in use. If a single cylinder supplies two or more users, the identities of the users in operation at any particular time should also be provided. A general inspection should be performed each time a gas cylinder is used in order to ensure that there are no obvious safety concerns. Each day or working shift, the last person to leave the laboratory should make sure that all cylinders are properly closed.

A.5 Safety checks before and during operation

Ensure that all safety interlocks function properly prior to using the instrument. Before the glow discharge is ignited and after the ignition for a while, the stability of the gas flow rate and pressure should be checked to be sure that adequate vacuum condition is being kept.

ICS 71.040.40

Price based on 8 pages