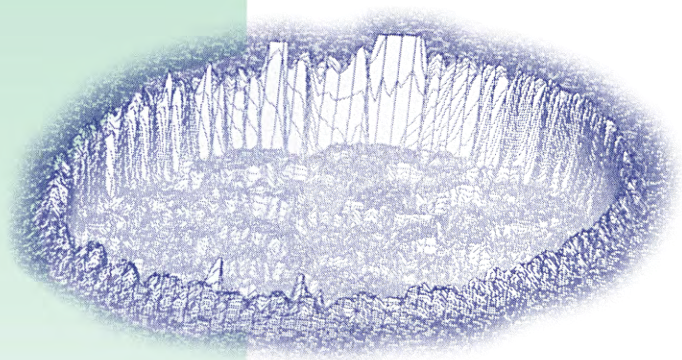


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Glow Discharge Optical Emission Spectroscopy: A Practical Guide

THOMAS NELIS *and* RICHARD PAYLING

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Glow Discharge Optical Emission Spectroscopy

A Practical Guide

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Glow Discharge Optical Emission Spectroscopy

A Practical Guide

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Preface

Glow discharge optical emission spectroscopy (GDOES) is an essential technique for the direct analysis of bulk solids, elemental surface analysis and the depth profiling of thin films and industrial coatings. This book is designed for all those using or managing GDOES instruments and for those who would like to know more about the technique from a hands-on perspective. It will also aid those considering the purchase of a GDOES instrument, or those using GDOES results, to understand in detail how the technique works and what is involved in maintaining the instrument and achieving high-quality results.

The book is designed as if the reader has just sat down at their instrument. It begins with checking whether the instrument is on and working correctly, then deals with sample preparation, method creation and optimisation of the instrument and source settings, then calibration and drift correction if necessary, followed by analysis (bulk or depth profiling) and the interpretation and presentation of results. Then follow additional chapters on the theory of GDOES, line selection, and trouble shooting.

The book may be read from cover to cover or the reader may prefer to skip to individual chapters of immediate interest. The theory chapter, for example, is largely self-contained and presents an up-to-date account of the glow discharge plasma, sputtering and quantitative analysis. Several chapters deal with calibration, probably the most challenging area for GDOES operators, including all aspects of calibration: the number and selection of calibration samples, the choice and optimisation of the calibration function, validation, and the calculation of uncertainties. The descriptions are not aimed at particular instruments or manufacturers and are therefore designed for use by everyone working in the field.

Throughout the book, we have endeavoured to follow ISO and IUPAC guidelines on procedures and nomenclature. At times these recommendations are crucial to analysis, as is the distinction between precision and accuracy. At other times, they are in conflict with common usage in GDOES. Where there is no reasonable ambiguity, we have opted for common usage. Hence, we have used content or composition, in units of mass% or atomic%, throughout in place of the more familiar concentration, now reserved for mass per volume, g L^{-1} . But we have continued to use voltage instead of potential difference when speaking about glow discharge source operation.

We would like to thank the series editor, Neil Barnett, for his suggestion and invitation to write this book, and for his useful comments on the draft manuscript.

We are indebted to our GDOES colleagues, Max Aeberhard, Philippe Belenguer, Arne Bengtson, Olivier Bonnot, Patrick Chapon, Volker Hoffmann, Paul Kunigonis, Mike Winchester, and Zdenek Weiss, for their many helpful comments on the draft manuscript.

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Finally, RP acknowledges the expert assistance of his wife Barbara Hoving in setting up the presentation style of the manuscript, and for her abiding support.

To dear colleagues Max Aeberhard and Paul Kunigonis

Contents

Chapter 1	Preparation and Maintenance of Instrument	1
1	Before Starting Measurements	2
2	Routine Checks	3
3	Monitoring Key Parameters Over Time	4
4	Anode-to-Sample Gap	5
5	Centring the Spectrometer	6
6	Window Cleanliness	7
7	Designing a Standard Test	8
8	Shutdown	9
9	Start-up and Shutdown Sequences	10
Chapter 2	Samples: Selection and Preparation	11
1	Sample Selection	11
2	Preparation of Bulk Samples	13
3	Surface Samples	16
4	Small Samples	17
5	Powders	18
6	Rods, Tubes and Wires	19
Chapter 3	Optimisation of Source and Analytical Parameters	21
1	Flush Time	21
2	Pre-burn (Pre-integration)	22
3	Integration (Averaging) Time	25
4	Precision: Internal and External	31
5	Memory Effects	33
6	Voltage, Power, Current, Pressure	33
7	Optimising Plasma Parameters for Bulk Analysis	37
8	Optimising Plasma Parameters for Depth Profiling	38
9	Sequence for Optimising Parameters	42

Chapter 4	Calibration	45
1	Introduction	45
2	Preparation for Calibration	48
3	Calibration Function	52
4	Regression and Uncertainties of Calibration Parameters	56
5	Confidence Levels of Calibration Curves	64
6	Outliers	72
7	Optimisation of Calibration Curves	74
8	Validation of Calibration Curve	74
Chapter 5	Calibration for Bulk Analysis	76
1	Calibration Types	76
2	Mini-Calibration (Type Standardisation)	80
3	Sequence for Calibration for Bulk Analysis	81
Chapter 6	Calibration for Compositional Depth Profiling	82
1	Sputtering Rate	83
2	Density	91
3	Linearity	93
4	Matrix Effects	94
5	Optimisation of Calibration Curves for CDP	95
6	Case Study: Galvanised Steel	99
7	Sequence for Calibration for CDP	102
Chapter 7	Drift Correction	103
1	What is Drift Correction	103
2	Selection of Drift Correction Samples	104
3	One Point, Two Point, Multiple Point	105
4	Uncertainties of Drift Corrections	107
5	Check When Required	108
6	Sequence for Drift Correction	109
Chapter 8	Bulk Analysis	110
1	Precision and Number of Replicates	111
2	Estimating Uncertainties in Analysis	113
3	Homogeneity	117
4	Accuracy	117
5	Grade Analysis	117
6	Presentation of Results	118
7	Case Study: Cast Iron	120
8	Sequence for Bulk Analysis	121
Chapter 9	Qualitative Depth Profiling	123
1	Near Surface	123
2	Coatings	127

3	Interfaces	129
4	Comparison of Intensity Profiles	132
5	Presentation of Results	133
6	Sequence for Qualitative Depth Profiling	134
Chapter 10	Compositional Depth Profiling	136
1	Mass %	137
2	Atomic %	137
3	Coating Weight	139
4	Uncertainty of the Calculated Depth in CDP	140
5	Presentation of Results	142
6	Case Study: Galvanised Steel	144
7	Sequence for CDP Analysis	145
Chapter 11	Theory	147
1	Plasma	147
2	Modelling the Plasma	150
3	Sputtering	158
4	Quantitative Analysis	163
5	Compositional Depth Profiling	164
Chapter 12	Line Selection	178
1	Wavelength Convention	178
2	GDOES Spectra	179
3	Best Analytical Lines	180
4	Interferences	183
5	Linearity, Self-absorption	184
6	Molecular Bands	185
Chapter 13	Troubleshooting	187
1	Diagnosis	187
2	Troubleshooting Guide	190
Further Reading		193
Appendix		194
	Appendix A: Most Used Optical Emission Lines in GDOES	194
	Appendix B: Additional Optical Emission Lines of Interest in GDOES	203
Index		209

CHAPTER 1

Preparation and Maintenance of Instrument

There are several different designs of GDOES instruments available on the market and they range in size from small bench-top units to large laboratory systems, depending mainly on the focal length of the spectrometer. The largest GDOES instrument ever built, one of the first but no longer made, had a focal length of 2.5 m. Today, spectrometers vary between 150 mm and 1 m in focal length. Despite these variations in size, they all have many features in common (shown in block form in Figure 1.1):

- glow discharge source
- optical spectrometer(s)
- vacuum pump(s)
- electronics
- computer and printer
- services: electricity, ultra-high purity argon

Some have additional services: water cooling, high purity nitrogen (for spectrometer), compressed air (for pneumatic valves) and a computer network/Internet connection.

Before beginning work on an instrument, the first thing to do is to check that each of these components is up and running. Walk around the instrument. Check that the area is tidy and the cables are connected. Check the services are working: electricity, gas(es) and cooling water. If necessary, check that the vacuum pump(s) is working. Check that the GD source is clean and ready and the computer is on. Run a common bulk sample for several minutes to ‘condition’ the source, *i.e.* warm and clean the source through normal operation. If necessary, check the alignment of the spectrometer(s). The instrument should now be ready.

Glow discharge spectrometers, like most analytical instruments, need regular maintenance and preparation for measurements. So, besides this initial inspection, consider regular maintenance checks. The purpose of maintenance is at least two-fold:

- to avoid serious trouble with the instrument and
- to avoid bad/wrong measurements

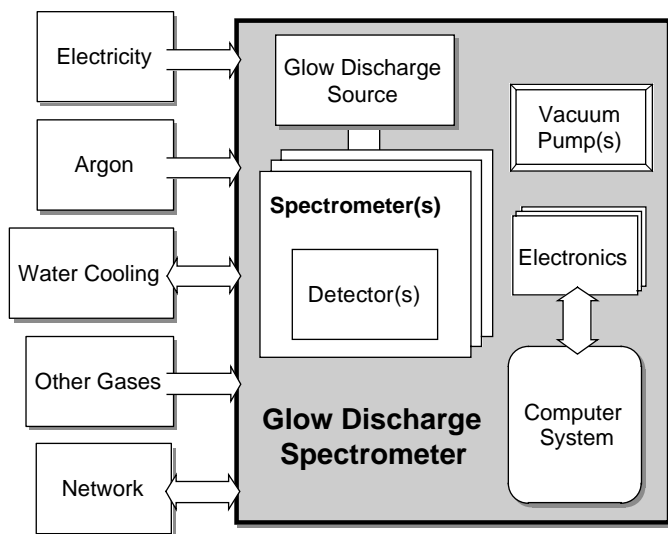


Figure 1.1 Block diagram of GDOES instrument

Checking the instrument before starting the analysis not only avoids trouble during the measurement, but also helps the operator to concentrate on the task of getting excellent results, as it liberates the mind from constant worries such as:

- Is my computer system stable?
- Is there enough argon?
- Do we have a leak in the source?

It is beyond the scope of this book to give detailed instructions for the maintenance of all instruments currently available on the market. For details on routine maintenance specific to your instrument, refer to the user's manual supplied with your instrument. In the following, we will provide general advice on maintenance procedures that will help save time in the long run and improve the overall quality of the analyses.

1 Before Starting Measurements

We will now consider preparation in more detail. Before starting to operate your instrument, make sure the computer and the software are in stable condition. This implies:

- if necessary, restart the system
- check the available space on the hard disk regularly
- archive the data you definitely do not want to lose

Checking the different supplies, such as gas, water and electricity, before starting analysis should become a habit. The argon supply pressure must be in the range specified by the instrument manufacturer. A different argon supply pressure may seriously affect the performance of the argon pressure regulation in the discharge chamber. When using gas bottles, be aware that the last 10% of the bottle may no

longer meet the quality required. When replacing argon bottles, avoid getting air into the argon gas line.

Make sure the cooling system(s) is operating properly:

- check the water supply for open (non-return) systems or
- check the level of the cooling liquid for closed (recirculating) systems
- check for particles in the closed cooling liquid; if necessary replace the liquid

Make sure no power failure has occurred since you last operated the instrument, as this may seriously affect the condition of the instrument. For example, a long time without power may have affected the thermal regulation of the spectrometer, so the instrument may need time to stabilise. A common guide for larger, heated spectrometers is 1 hour stabilising time, up to a maximum of 8 hours, for each hour without electrical power.

When the instrument has not been used for some time, it is generally recommended to run a few dummy samples, before optimal stability can be achieved. This effect may be more or less important, depending on the design of the instrument.

2 Routine Checks

Perform regular routine analyses on samples of known chemical composition. If your instrument is used for depth profiling, these samples should include homogeneous reference materials as well as coated materials (see, *e.g.* Figure 1.2).

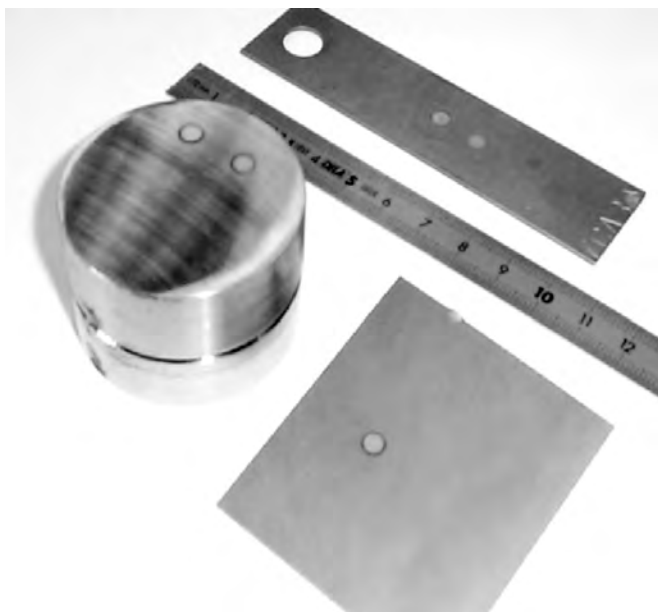


Figure 1.2 Typical samples used for routine instrument checks: recal steel sample rich in C, S and P for checking window cleanliness (left), zinc phosphate-coated steel for O sensitivity (top) and galvanised steel for sputtering rate (bottom) (scale in cm)

The purpose of these tests is to assess, verify and finally establish in written or recorded form the current performance of the instrument. They also help to detect possible malfunctions of the instrument, prior to analysis. Another result of routine checks on samples of known composition is the possibility of measuring the long-term precision and accuracy of the instrument for a given application, and the frequency required for drift corrections.

For bulk analysis, we suggest you analyse two different homogeneous samples, one a low-alloyed material and the other a high-alloyed material. The chosen materials should have a large number of specified elements. In particular, the elements contained in air, namely N, O, C and H, should be checked to make sure no air leak has occurred, as only a small amount of air in the discharge chamber can drastically change the nature of the glow discharge plasma, for all elements.

Analysing a coated sample allows you to monitor the sputtering rate and depth resolution. The sample used for routine checks should therefore be homogeneous in coating thickness and should have clearly defined interfaces between the different layers.

3 Monitoring Key Parameters Over Time

To monitor the performance of the instrument and to detect malfunctions before they become significant in the analytical results, the following key parameters should be monitored over time:

- intensities
- source impedance

An example is shown in Figure 1.3. These charts allow quick troubleshooting and can be used to plan preventative maintenance, thereby reducing unscheduled downtime.

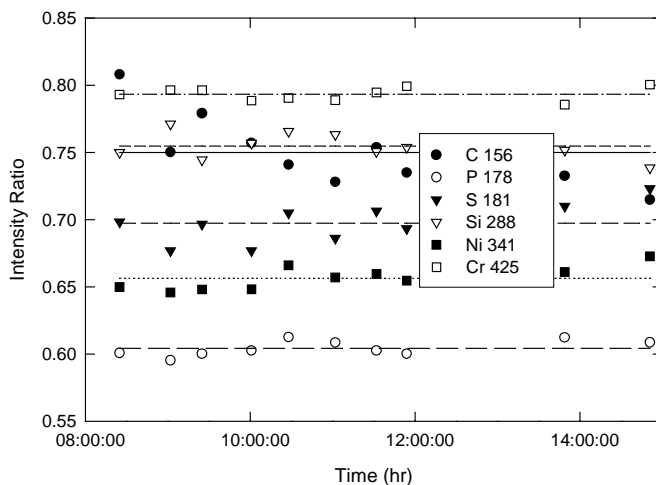


Figure 1.3 Run chart for changes in intensity over time: here a cast iron sample is measured repeatedly over several hours, with intensities ratioed to iron. This type of measurement could be repeated over days, weeks or months, to see long-term trends

Monitoring the intensities of the elements, N, O, C and H, over time, if they increase significantly or suddenly, can help detect air leaks in the argon supply system. All the wavelengths shown in this book are in nanometre (nm).

Monitoring the impedance of the GD source for a given sample can be used to record the reproducibility of the plasma, *i.e.* of the sputtering and excitation processes. In particular, it can be used to monitor the pressure regulation and any changes in the anode-to-sample gap over time, with the eventual need to replace the anode if the gap becomes too large. Changes in source impedance can be monitored, in RF operation, at fixed applied power and pressure by recording changes in the DC bias voltage or applied voltage over time. In DC operation, the voltage can be recorded at fixed current and pressure.

4 Anode-to-Sample Gap

The anode-to-sample gap is one parameter that has generally been neglected in most work on glow discharge spectroscopy. Though it is not so difficult to measure, no manufacturer currently provides a routine way of doing it. Despite this negligence, the anode-to-sample gap is a crucial parameter for reproducible GDOES data. Increasing the anode-to-sample gap increases the source impedance. This change in source impedance then affects the relationship between current and voltage in the plasma. The effect is shown in Figure 1.4 for a large change in anode gap from 0.12 mm to 0.30 mm. Such a change, if undetected, would have dramatic effects on the validity of calibration curves and the accuracy of analysis.

An anode-to-sample gap between 0.08 mm and 0.2 mm is generally recommended. Small gaps are usually beneficial for improving depth resolution; larger gaps allow running the discharge for longer times without creating a short circuit between the anode and the sample. Whatever gap is chosen by the manufacturer or the operator,

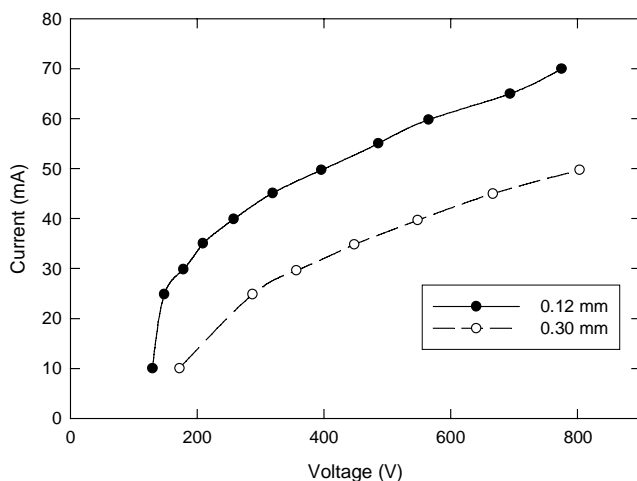


Figure 1.4 Effect of changing anode-to-sample gap, from 0.12 to 0.30 mm, at constant pressure



Figure 1.5 *Micrometer screw gauge adapted for measuring the anode-to-sample gap¹*
(Reproduced with permission from John Wiley & Sons)

it should be kept constant for a given type of analysis. Variations in gap size will lead to variations in glow discharge conditions and thereby alter the analytical results.

The anode-to-sample gap can be measured with a specially adapted micrometer screw gauge (see Figure 1.5). Ideally, it should be capable of measuring the gap to within $\pm 10\text{ }\mu\text{m}$. If no such device is available, one way of suspecting that the gap is getting too large is that it becomes more difficult to get flat craters, especially with typical source conditions.

5 Centring the Spectrometer

GDOES instruments containing a polychromator(s) built on the Paschen–Runge design, with a movable entrance (primary) slit, fixed exit slits and photomultiplier tubes as detectors, need occasional centring of the primary slit. This generally means the entrance slit of the spectrometer is moved to give maximum intensity on one specific line. The result is that all other lines on the polychromator will also be centred simultaneously. How well this works depends on how well the secondary slits were aligned during manufacture of the spectrometer. An example is shown in Figure 1.6.

Depending on the design of the spectrometer, this operation needs to be performed every day, occasionally or only once the polychromator has been opened. It is a good practice to use the same conditions (method) and the same sample and to note the changes in peak position and intensity. This will indicate if there is a problem in the spectrometer, such as change in temperature, or if the window needs cleaning.

Scanning monochromators in the Czerny–Turner design also require occasional alignment, because of the movement of the grating, typically using the zero-order reflection from the grating and argon reference lines. A useful argon reference line is at 415.859 nm.

Spectrometers using CCD detectors to cover wide ranges of the spectrum generally do not need this operation, as it can be integrated directly in the mathematical algorithms used for line identification. Nevertheless, the assignment between pixel number and wavelength should be checked from time to time and, if there are systematic errors, a new function should be applied.

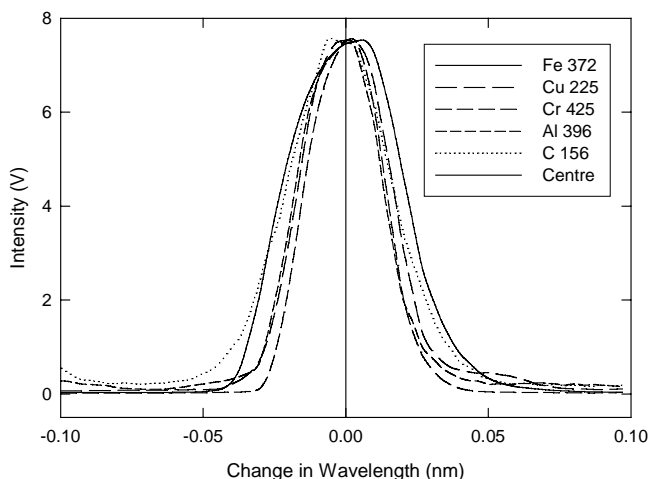


Figure 1.6 Example line scan for Fe 372 from a steel sample used for aligning the polychromator; showing that other lines on the polychromator are also aligned simultaneously

6 Window Cleanliness

Monitoring intensities over time for selected elemental lines covering a wide range of wavelengths allows checking the performance of the optical spectrometer. A continuous decrease of all intensities, being most severe at short wavelengths, would indicate increasing pollution of the optics, particularly the window between the glow discharge and the optical spectrometer. An example is shown in Figure 1.7. In this example, the intensities of the many lines on a polychromator were measured for two samples, Zn–Al alloy Canmet ZN3 and Steel NBS 1262, soon after cleaning the window and then 3 weeks later, after analysing a large number of other samples, including many paint coatings. The intensities after 3 weeks were then divided by the intensities with the clean window. After seeing these results it was decided, for this particular instrument, to clean the window every week. For other instruments analysing other materials, it is common to clean the window only once a month, or even less frequently. This decision will vary from laboratory to laboratory and is best decided from experience and from data over time.

Contamination of the window can occur from sputtered material. Grimm-type sources are designed to have a counter-flow of argon that travels across the window and is then directed towards the sample to minimise deposition on the window. Sometimes pollution comes from the oil pumps used in the source, and sometimes from the evaporation of low-temperature samples, *e.g.* tin or lead. Oil will tend to accumulate in places with the lowest temperature. Clearly, the source should not be at the lowest temperature in the pumping line. Additional pollution can come onto the back of the window from the outgassing of inappropriate sealants inside the spectrometer, and in vacuum spectrometers, from back streaming oil from vacuum pumps.

A common question is: how often to clean the window? As suggested above, there is no general answer, because of variations in source designs and varying workloads

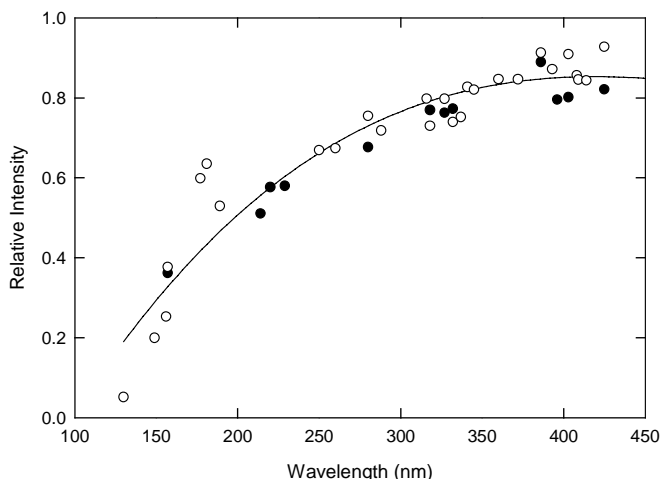


Figure 1.7 *Change in intensity of the many lines on a polychromator after 3 weeks:*
 • Zn-Al alloy ZN3, ○ carbon steel NBS 1262

on instruments. But the best approach is to monitor changes in intensities at various wavelengths over time, *e.g.* in run charts. Always use the same experimental conditions (method) and the same samples. If intensities are dropping, it is probably due to a dirty window. Cleaning the window should restore intensities to their earlier values. After a while, it will become clear how often cleaning is necessary.

Sometimes operators have noticed intensities drop quickly soon after cleaning the window and then more slowly. Under these circumstances, they prefer to clean less often, *i.e.* to accept lower intensities in exchange for long-term stability. Clearly, in these cases there is a source of pollution that only slightly covers the window. In an ideal world, it would be better to fix the source of pollution than accept lower intensities.

7 Designing a Standard Test

After these general considerations on checking instrument performance, many readers might now expect us to provide them with a plan for their routine checks, defining which parameters must be checked and how often. Considering, however, that there is really no such thing as a ‘good’ or ‘bad’ instrument, but just instruments that either meet specifications or do not, it is rather difficult to write such a general document.

International Standards Organisation (ISO) standard 10012 requires that all measurement tools, *i.e.* those used for serious measurement, must be checked to see whether they meet the requirements for the task or not.² These checks must be performed at regular intervals. The nature of the checks and their check interval must allow the user to assure that the measurement tool is adequate for use.

For a GDOES instrument, this means that all physical properties that may influence the analytical results, and we have identified many of them in this chapter, must be checked on a regular basis. To avoid spending more time checking the instrument

than doing analysis, it is sensible to choose the intervals to be as long as possible. It is therefore suggested to monitor key parameters on a daily basis when the instrument is new. As the amount of data increases, you can derive new, hopefully longer, intervals based on the variations in parameters, their influence on the final analytical result and your analytical requirements (precision and accuracy). This ensures that you meet ISO standards, and that your analytical results are as good as you need them to be.

8 Shutdown

There are two approaches for shutting down an instrument for the night:

- Leave everything on, on the basis that being on promotes thermal stability and minimises interruptions and possible power spikes.
- Turn off as much as possible, on the basis of saving energy and prolonging life by minimising use.

Each has its advantages and disadvantages. Leaving everything on will mean:

- fast start up in the morning
- possibly a more stable instrument, but
- more prone to power outages overnight
- more pollution from the oil pump(s)

The disadvantages can be minimised by ensuring the instrument will restart correctly after a power failure, and by having a small argon leak into the pumps to reduce the back diffusion of oil. Note that not all instruments use oil pumps.

Turning most things off will mean:

- saving energy
- possibly extending the life of the instrument, but
- possible damage from surges during start up
- slower start up in the morning, especially waiting for the oil pump(s) to reach equilibrium temperature (typically 1 hour)

The disadvantages can be minimised by always starting in the same sequence and by having oil pumps turn on automatically with a timer about 1 hour before starting work.

Whichever approach is adopted, it is advisable to keep the source closed overnight, to reduce contamination of the source by air and moisture, which could then affect early analyses the next day. This can be done by placing a flat sample (*e.g.* a glass slide, a small metal sheet or the cooling block, if appropriate) on the source and then closing the valves to the pump(s) so that the source is left under vacuum but without argon and without being pumped. The pump(s) may then be turned off if you wish. This exact procedure may not be possible on all instruments but it should be possible to place some form of temporary cover on the source overnight. Check that the procedure used does not mean that a large quantity of argon is being consumed all night.

Nitrogen-purged spectrometers should be kept purged overnight; large vacuum spectrometers should be kept evacuated overnight. Should it be necessary to stop the nitrogen or vacuum pumps, perhaps for other maintenance in the laboratory, care should be taken when switching off the instrument to ensure the spectrometer is left in a suitable state. Refer to your user's manual. Later, when restoring the instrument, purging or evacuating the spectrometer to a level where intensities in the far UV are stable may take several hours. It may also take some hours for the spectrometer to reach a constant temperature, in particular when the operating temperature of the spectrometer is above the temperature of the laboratory environment.

For vacuum spectrometers, intermediate pressures, *i.e.* pressures between about 10 and 10 000 Pa (0.1 and 100 mbar), are dangerous for photomultipliers, because a glow discharge can be ignited around the tubes at the high-voltage supply connection. Normally, the electronics does not allow the high voltage to be switched on at these pressures. During pump-down, therefore, high voltages to the spectrometer should be switched off.

9 Start-up and Shutdown Sequences

The following steps are recommended for routine *start up*:

1. check gas supplies, *i.e.*, argon (and nitrogen)
2. check water supply for open systems or check level of cooling liquid for closed systems
3. run a common sample for several minutes
4. centre polychromator, if needed

The following steps are recommended for routine *shutdown*:

1. if possible place a light, flat sample or cooling block on the source, evacuate and close valves to pump(s), otherwise place a cover over source opening
2. if turning off source vacuum pump(s), turn off pumps
3. if necessary turn off argon
4. keep spectrometer either evacuated or with nitrogen

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