4

ROUTINE MAINTENANCE

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Forewords

Recent technologies let us build up instruments that require less maintenance as in the past time.

Some parts of the instrument, mainly the stand, are more subject to be used and it remains necessary to proceed to some operations that we call **routine maintenance**. These operations are usually performed by the operator at regular intervals, or their frequency is depending on the sample throughput.

In order to guarantee a long term operation with a minimal breakdown risk, as well as to keep the initial analytical performances, it is highly recommended to overhaul completely the instrument at regular intervals, for example once a year. This is called the **service maintenance**; that should be performed by an Thermo Fisher Scientific– or agreed local agent – service engineer.

Operations and procedures concerning the **service maintenance** are developed in the *Service Maintenance Manual*, which is foreseen for Thermo Fisher Scientific– and agreed agents' – after-sales personnel. Hereunder in this chapter, we will only talk about a **routine maintenance** guide foreseen for the operator.

Note: The **standardisation** (sometimes also called **recalibration**, or even normalisation), is considered by some people as part of the routine maintenance. However we will not develop this subject in this chapter. You can find explanation and procedures about the standardisation in the *Analytical Principles* chapter of this manual.

Application Domains of Procedures

The routine maintenance procedures described in this chapter can be applied to most current application cases.

In some particular cases, especially in domains requiring ultimate performances, different or more rigorous procedures are necessary to achieve those performances.

For the particular application domains listed below, you must first consult the *Special Procedures* appendix of this manual. This appendix shows the differences of procedures in relation to the ordinary procedures of this chapter.

- **Magnesium alloy matrix**

For the maintenance of the material for the analysis of VUV elements, the *VUV Line Analysis* manual must also be consulted.

For all other cases not explicitly mentioned, the routine maintenance procedures described in this chapter must be applied.

Summary Table

The few routine maintenance checks to be carried out periodically are pointed out in the table hereunder. Further detailed explanations follow in the next sections of this chapter.

Maintenance subject	Recommended frequency
Cleaning of the electrode	Before each analysis
Replacement of the electrode	Every 62'000 runs
Quick cleaning of the table and the sparking chamber	Every 1250 runs or at least once a day
Cleaning of the insulator and the sparking chamber	Every 5000 runs or at least once a week, before standardisation
Cleaning inside the stand (table, block support)	At least once a week
Argon outlet filter	At least every 1250 runs
Check pump oil level	At least once a week
Change vacuum pump oil and gaskets	Every 6 months
Profile check	Monthly (at first weekly)
Greasing of stand's door hinges	Once a month
Lens cleaning	Once a month
Cleaning the dust filters Changing the dust filters	Once a month Once a year
Operation of cabinet fans	Once a week
Running Control Sample and/or Standardisation	Once a day (optional) Once a week
Backup	Once a week
Accessories in option	According to manufacturer

Note: The cleaning of the lens, the profile check and the vacuum pump oil change, even taken separately, can considerably affect the response of the instrument; they must thus be followed by a standardisation and must be carried out before the standardisation started.

We recommend a waiting time of about 15 minutes between the cleaning of the lens and the standardisation. This delay is necessary to flush out the air that is entered into the sparking chamber and pipes during the cleaning. This delay can be reduced if the pipes and the chamber are purged with the analytical flow rate, by choosing the direct profile mode for example.

Analysis Electrode

The electrode should be cleaned with the small metal brush before (or after) each analysis.

Take care to not worn the analysis table and the border of the analysis hole with the brush.

A quick cleaning of the surface of the table is also advised, in order to remove metal dusts or possible greasy deposits from fingers. Do it with a soft brush or a dry rag, lightly moisten with alcohol.

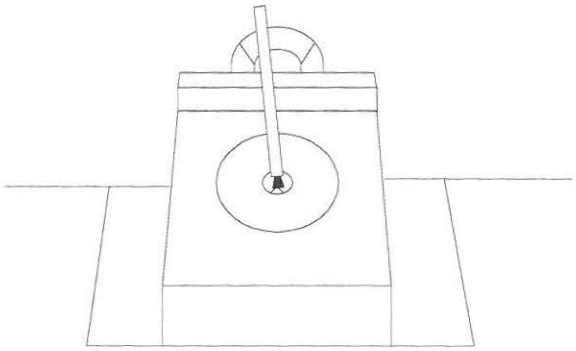


Figure 4.1

A worn metal brush does not do its job properly and must be replaced. Only use the brushes supplied by Thermo Fisher Scientific.

Your experience can bring you to the conclusion that an electrode cleaning is not necessary after each analysis, but only perhaps after every 10, 50 or even 100 analyses, the choice is yours. By cleaning the electrode after each analysis, you ensure a greater accuracy. It is necessary to clean the electrode when you change the type of alloy analysed, and also between each sample during the standardisation or calibration of a new method.

Electrode Exchange and Adjustment

If the electrode's tip becomes rounded, or if it breaks off, it must be replaced. Nevertheless we recommend to exchange the electrode every 62'000 runs. Use only electrodes supplied by Thermo Fisher Scientific.

Even if it is not necessary to replace the electrode, it is useful to check its adjustment by time to time.

By loosing the clamping screw (see ②, figure hereunder) the electrode automatically lifts up. You can then take it out with your finger or pliers. If the electrode does not lift up by itself, we recommend to change the complete module (by a Service Engineer).

The electrode adjustment is done with a 3 mm gap gauge that is supplied with the instrument (see figure hereunder):

① Press with one hand on the gauge in order to push down the electrode into the cylinder,
② Tighten the clamping screw.

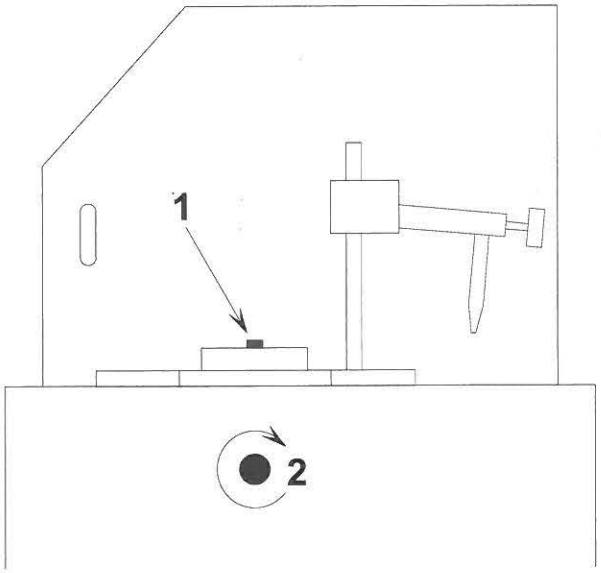


Figure 4.2

Cleaning of the Stand and the Sparking Chamber

The sparking chamber is the argon flushed space inside which the electrical discharge between the electrode and the sample takes place.

The sample material burned by the discharge lefts a dusty blackish deposit. A part of this deposit is evacuated through the argon pipe towards the argon outlet filter. It is necessary to remove the remaining dust deposit from the chamber regularly.

Quick cleaning of the Table and the Sparking Chamber

We recommend to do a quick cleaning of the table and the sparking chamber every 1250 runs, or at least once a day or at each shift change. This should not take more than one to two minutes. The frequency can be modified according to the metals analysed and the analytical condition.

It is absolutely not necessary to release the analysis table nor to dismantle any other part of the stand during this operation. Using a vacuum cleaner, cover around half the table's hole with the nozzle for a maximum of 1 second. Repeat this operation 3 times, but not more.

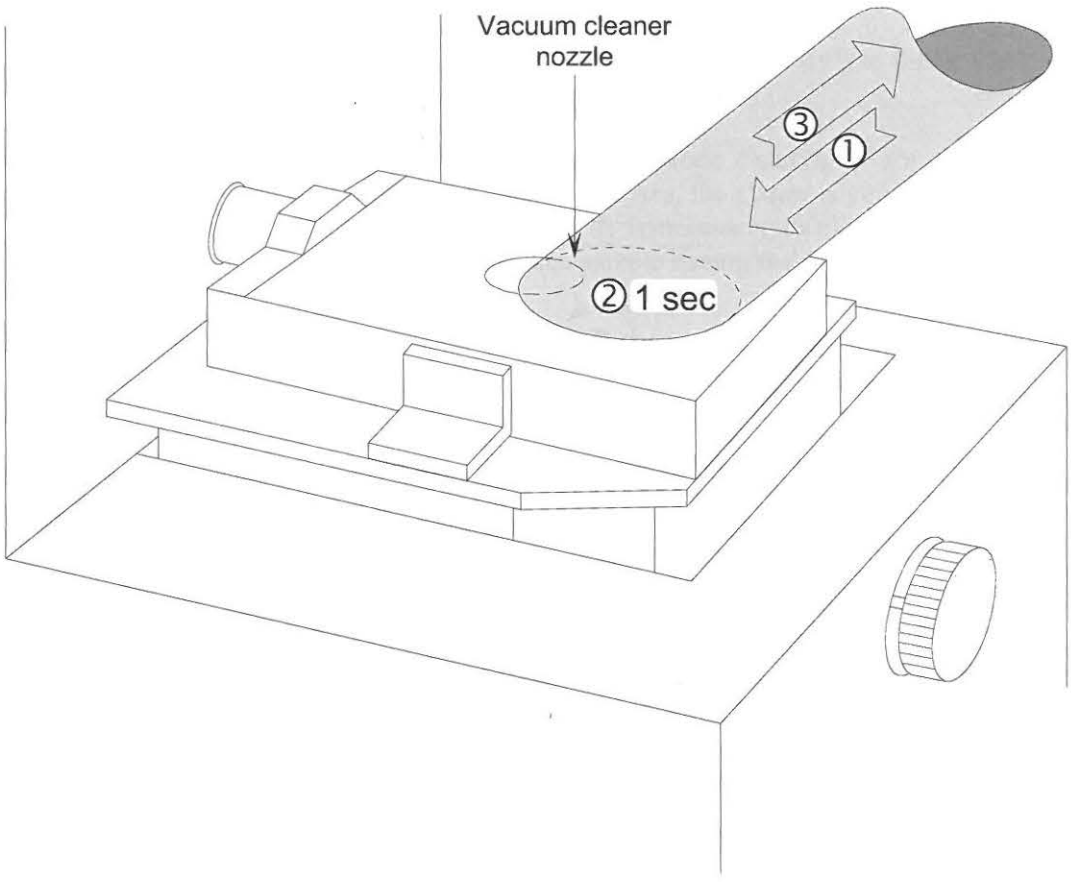


Figure 4.3

Never cover the analytical hole completely, otherwise the metallic dust will be sucked out from the outlet filter through the pipes, and do not aspirate more than one second at a time.

Note:	After this cleaning you should make about 5 runs with a conditioning sample.

Cleaning of the Insulator and the Sparking Chamber

We recommend that these jobs be carried out every 5000 runs, but at least once a week before the standardisation.

However if your sample throughput is high, fast intermediate cleaning can be carried out. If these cleaning sessions are carried out with care, they will not affect the instrumental response, so an intermediate standardisation will not be necessary.

Remark: If the instrument is used for analysing various matrixes (bases), it is necessary to change the analytical set (analytical table, electrode, brush, insulator) for each matrix change. Therefore analytical sets must be kept separately and not mixed.

For removing the table, free the camlock screws.

Slightly lift up the table, and pull softly towards you. The table becomes free from the optical primary channel.

Warning! By acting too abruptly you may break the electrode.

Remove the o-rings of the base plate – before they have been aspirated by the vacuum cleaner!

Remove the glass insulator by lifting it (take care not to break the electrode tip) and clean it first with a vacuum cleaner, eventually with a piece of rag slightly moisten with alcohol so as to remove greases.

After the insulator is removed, remove the dust of the sparking chamber with a vacuum cleaner. Here again take care not to hit the electrode tip. A broken electrode must be replaced.

Once these cleanings are done, put everything back into place and put a sample on the table so as to cover the analysis hole.

Note: The oxygen in the air perturbs the creation of the plasma during the sparks. This is why we recommend that you always leave a sample covering the analysis hole (see also *Remarks*).

Cleaning of the Table and the Inside

In this section we consider the analysis table and the inner space of the table's block support.

We recommend a weekly cleaning of these items. But here again, in case of a high (or low) sample throughput, the frequency must be adapted to the use of the instrument.

Dismantling

For removing the table, free the camlock screws.

Slightly lift up the table, and pull softly towards you. The table becomes free from the optical primary channel.

Warning! By acting too abruptly you may break the electrode.

Remove the o-rings of the base plate – before they have been aspirated by the vacuum cleaner!

Unscrew the electrode clamping screw (see ② of the figure 4.2), the released electrode should lift some millimetres. Take out the electrode, simply by pulling upwards with fingers.

Cleanings

Table's Block Support

Remove the metal dusts with a vacuum cleaner, if necessary with the help of a soft brush.

Electrode

The electrode brushing is explained in the section *Analysis Electrode*.

Analysis Table

Remove the metal dusts with a vacuum cleaner, if necessary with the help of a soft brush. Use pipe cleaners for cleaning the inside of the primary optical channel and the other inner pipes. Do not use solvents.

The top of the table can be cleaned with a piece of rag slightly moisten with alcohol. Nevertheless avoid the alcohol to pass on the inside of the table, or on the bottom part of it.

Note: The presence of water in the cleaning solvent has bad effects on the sparks. The alcohol used must then be very pure, or you must use isopropyl alcohol containing less water.

Glass Insulator

The glass insulator can be cleaned, for example with alcohol. It has to be put back only once dry!

Finally clean and dry all parts with paper towels and arrange them on clean papers.

Reassembling

Put back together everything in the dismantling reverse order, take a particular attention:

- to check if you don't forget to put back the o-ring of the table's block support,
- to put back the glass insulator,
- to insert well the front of the table around the primary channel's end,
- to close the table's camlock screws without forcing them, otherwise it indicates that one of the pieces is not in its place.

Check the electrode height adjustment with the gauge supplied with the instrument (see procedure in section *Analysis Electrode*). Tighten the clamping screw normally, without forcing.

Cover the analysis hole with a sample.

Remarks

The oxygen in the air perturbs the creation of the plasma during the sparks. This is why we recommend that you always leave a sample covering the analysis hole.

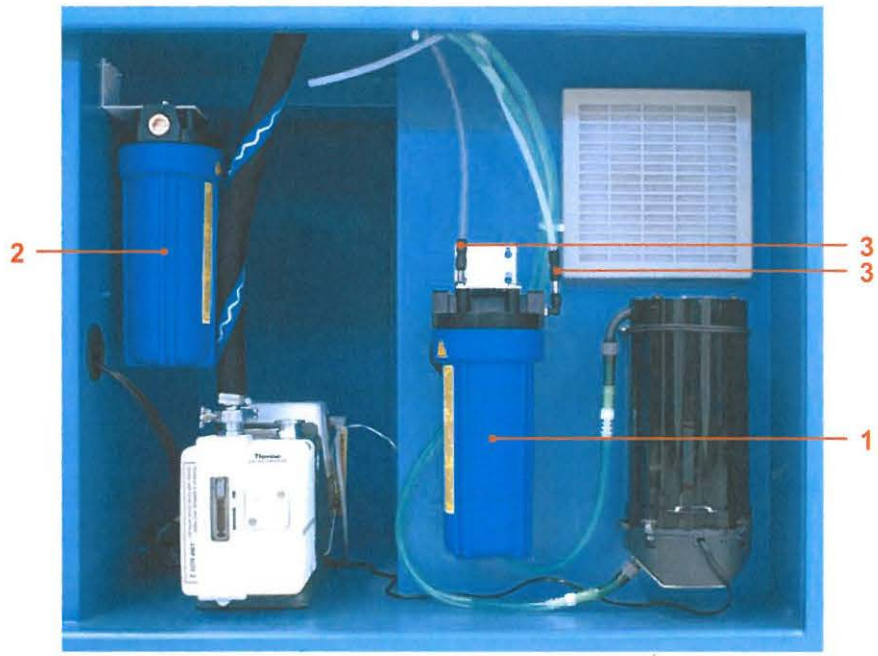
Like wise, during the maintenance operation and depending on how long it takes, air enters the sparking chamber and the argon pipes. It is possible that the first two or three attacks on the sample (the attack being the physical result of all the sparks of a measurement on the sample's surface) are insufficient (white or very pale attacks) to allow an accurate measurement. If the problem persists one must nevertheless remember there are many different reasons for bad attacks; the reasons can also be:

- bad argon quality,
- leaks in the pipes,
- defects in the sparking source's electronics,
- a bad sample which has inclusions of oxygen or another gas.

Argon Outlet Filter

If the instrument is used for Mg base analysis, it must be equipped with a special filter for Mg. In this case the directions in this section are not valid, please consult the *Magnesium base alloys* section of the *Special Procedure* appendix.

The argon outlet passes through a filter cartridge in a container. This device takes place in the centre back of the instrument as shown on the next figure.



1. Outlet filter
2. Spare filter (clean)
3. Fast fittings

Figure 4.4

Clean the cartridge and the container every 1250 runs.

A clean spare filter allows to operate the instrument immediately after a quick filter exchange.

Filter exchange

You can proceed to a fast filter exchange in the following way:

- Remove the spare (clean) filter ② from its waiting position.
- Disconnect the fast fittings ③ from the (dirty) outlet filter ①.
- Remove the outlet filter ① from its working position and leave it on the waiting position.
- Put the clean spare filter on the working position.
- Connect the argon inputs and outputs pipes ③ on the clean filter.

The instrument can be used immediately.

Filter cartridge and container cleaning

The synthetic filter cartridge retains the metal dust. **A fast input of air is likely to ignite fire on the filter**. In order to prevent fire ignition, follow the directions given below.

- Once the filter is placed on the waiting position the container must be unscrewed a little bit and slowly from its support of about one and half turn, if necessary, with the adequate supplied key.
- Wait 4 hours so as to let the dust oxidise (passivate) slowly.
- Finally unscrew completely the container in order to proceed to the cleaning.

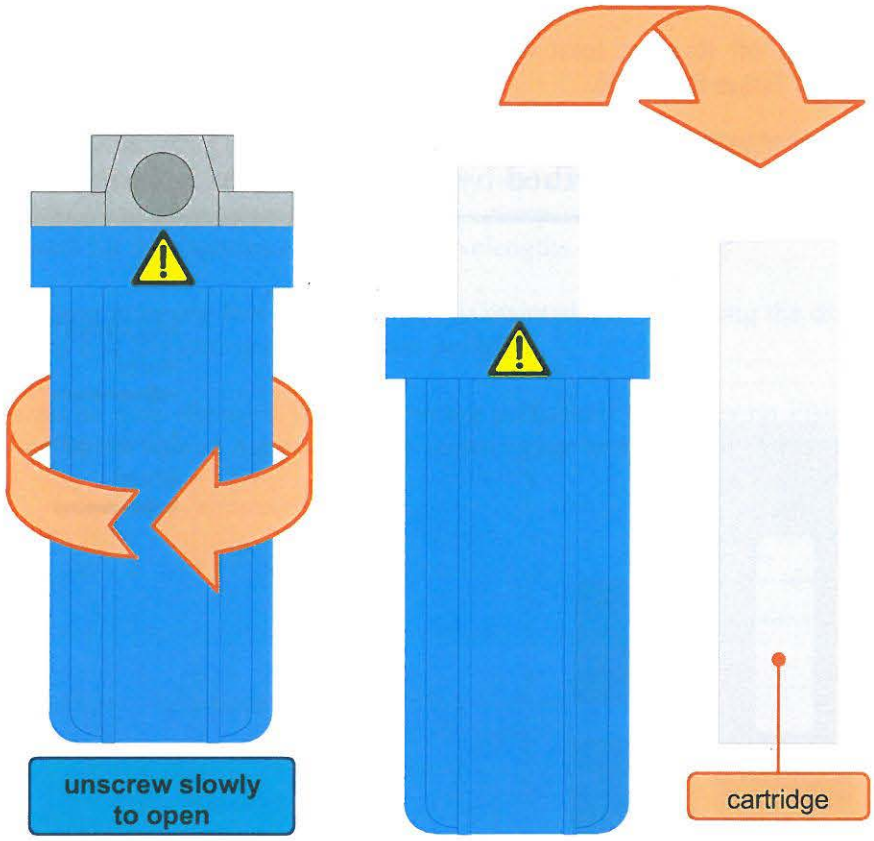


Figure 4.5

The filtering cartridge and the container are cleaned with a vacuum cleaner. When the cartridge becomes very dirty, it should be replaced.

After cleanings, put back all parts and place the clean filter as spare on the waiting position.

Vacuum Pumping Line

Depending the kind of pumping line installed, the maintenance is different. Two cases can be applied:

- a standard pumping line for an intermediary vacuum using an oil vacuum pump, without the VUV option, see later section *Standard Pumping Line for Intermediary Vacuum*.
- a special pumping line for a high vacuum, with a diaphragm pump and a molecular drag pump, for the VUV option, see later section *Special Pumping Line for High Vacuum*.

Standard Pumping Line for Intermediary Vacuum

Checking the Vacuum Pump Oil Level

Check the vacuum pump oil level at least once a week. If necessary top up the oil. Only use oil recommended by Thermo Fisher Scientific.

Use only oil prescribed by Thermo Fisher Scientific.

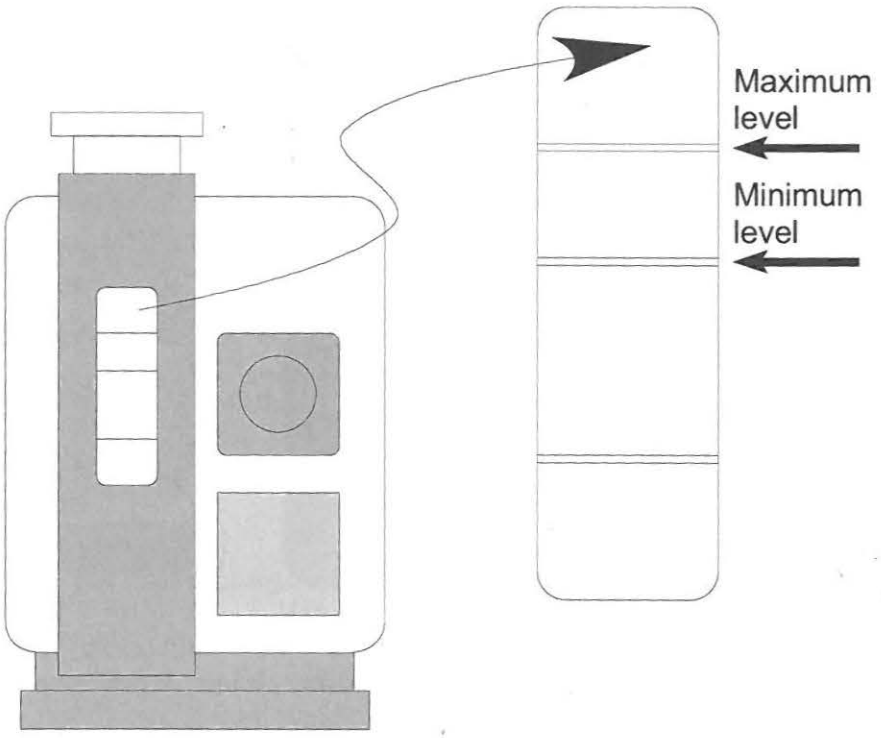


Figure 4.6

The oil level can be observed more easily if the pump is stopped – for a short moment – but still warm.

For oil addition, kindly refer to the pump supplier's manual that has been delivered with the instrument documentation.

Note: The pump performances and its life span are optimal when the oil level is between the maximum level and the minimum level.

Changing the Oil and the Vacuum Pump Gaskets

This operation is recommended every six months. The procedure is described in the pump supplier's manual that has been delivered with the instrument documentation.

Use only oil prescribed by Thermo Fisher Scientific.

Only the gaskets recommended by Thermo Fisher Scientific should be used. Your local Thermo Fisher Scientific after sales service (or our agreed agents) are at you disposal for the supply of spare oil and gasket kits.

These operations can be carried out upon request, during a service maintenance visit by one of our service engineers.

Special Pumping Line for High Vacuum

This system is necessarily mounted with the VUV option. This dry pumping line is derived from the Alcatel Drytel system and adapted to our instruments. A primary vacuum is made by the diaphragm pump. Then a molecular drag pump – located between the diaphragm pump and the spectrometer – is making the high clean vacuum necessary for the analyses of very low wavelengths spectral lines.

This special high vacuum pumping line requires a yearly maintenance (replacing the diaphragms and valves of the diaphragm pump and lubricating the molecular pump).

These operations must be done during a yearly servicing performed by a Thermo Fisher Scientific Service Engineer (or from one of our agreed Agents). Kindly contact your local Thermo Fisher Scientific Service.

Profile Check

The ARL 3460 is a very stable instrument. The profile's drift should be very slow and almost imperceptible However, we recommend that you check the instrument's profile at least once a week, at the beginning anc that the mean positions of the elements whose profile you have checked be kept in writing (with the dates the profiles where taken). By observing the evolution of these values, you will be able to judge for yourself if you can space out the profile checks (once a month for example).

The profile check of an element consists of finding the mechanical position of the secondary slit of this element relatively to the primary slit which is common to all of the elements (channels) installed in your instrument. The position of the primary slit is given by the graduation of the scanning dial.

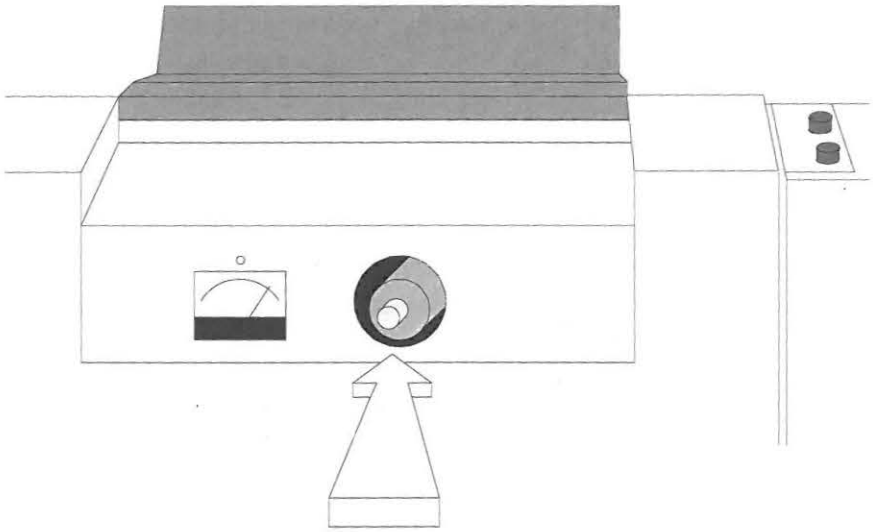


Figure 4.7

Your instrument has been profiled in our factory with the greatest care and all the secondary slits have been positioned mechanically to correspond with one single position of the primary slit. For analytical and mechanical reasons, all the elements do not require the same positioning precision. As a general rule, all the secondary slits are placed in an interval corresponding to ± 1 dial division of the average position.

There are two ways to take the profile: the first is called **direct** profile (or **manual** profile) and is an analogue way, the second is called profile **by integration** and is a digital way. The manual method is often faster and just as accurate as the integration method if care is taken. Nevertheless the manual method is more subject to error than that by integration as it calls for interpretations (and analogue readings on a multimeter) by the user.

The commands from the software for taking the **direct** profile or the profile **by integration** are under **Check Optics** of the **Tools** menu.

You will find the procedures of both methods as well as complementary theoretical explanations in the OXSAS contextual help. Hit the F1 key when the direct profile or the profile by integration dialogue is open to get the contextual help.

We only give hereunder some basic advices and recommendations for each of the two methods.

Direct (or Manual) Profile

We recommend that you take the profile regularly on three channels (elements) distributed regularly in the working wavelengths range of your instrument (i.e. to check the position of 3 secondary slits distributed over the slit holder's secondary slit frame). Always use the three same channels and note the profile positions found in your profile log book. Feel free to check one or several other channels now and again.

Choose channels (elements) which are relatively "easy" to profile. For a method with Fe base, take C (Carbon) for example, the (or a) standard Fe (Iron) and Al (Aluminium). In principle, these three channels cover the secondary slit frame well (one short wavelength, one medium and one long). If you have no experience of this, avoid channels S (Sulphur), P (Phosphorus) and Pb (Lead) which are difficult to measure. If you do not have a Fe base, request advice from the service engineer who installs your instrument.

A homogeneous profiling sample should be selected. It should contain a sufficient concentration of element to be profiled, so that the maximum profile response on the readout multimeter is at least at 80% of a full scale. You can change the scale's sensitivity among four choices by moving the sliding knob of the vacuum and profile board. Keep in mind the bar has 6 positions, two of them are for vacuum reading and measurement.

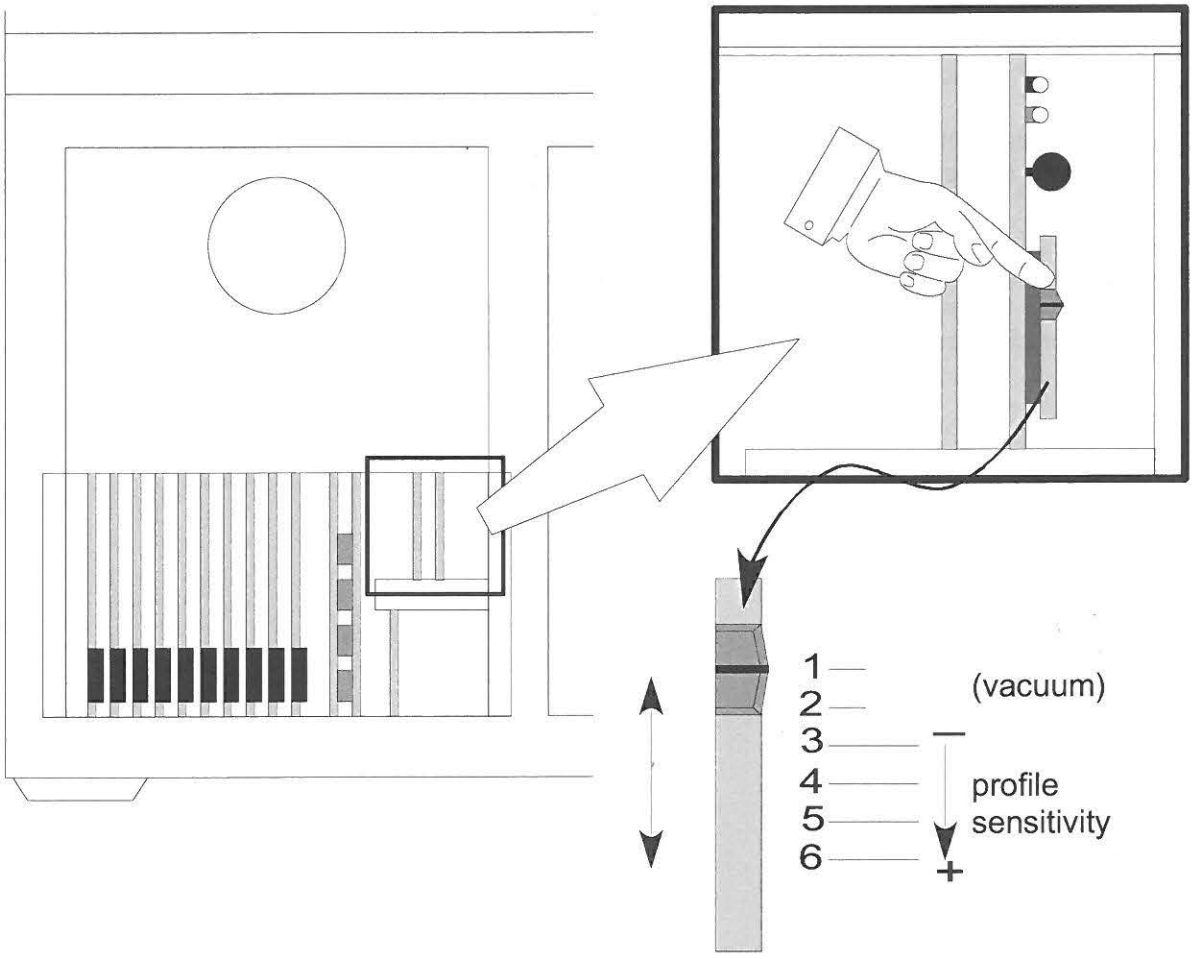


Figure 4.8

It is preferable to always use the same sample. It is not necessary to use a certified standard, nor a standardisation sample. It just has to be relatively homogeneous, contain enough of the elements to be profiled and its surface preparation must be correct.

The software will request the source conditions (of the sparks); use a condition specially created for the direct profile taking and always keep to the same one.

Note: If such a condition still does not exist, you must create it. Name it **PROFILE** for example, and copy the parameters of another standard condition, but change the integration time; you should enter a sufficient large time in order to let you to take the profile, for example 150 seconds.

The profile position must be taken quickly, but nevertheless care must be taken to perform this important task properly. The source operates permanently and it is not advisable to overheat the sample too much, nor to form a crater in it. With practice you will only need a maximum of thirty seconds to find the profile position of an element (some elements are volatile in the sample and you will have to be faster).

The analogue deviation of the direct profile – watched on the multimeter – is not always very stable and this is quite normal. This is where your experience and your judgement take on their importance.

Profile by Integration

The profile by integration is more simple, but in principle longer than the direct profile. The disadvantage is that the software does not have enough intelligence to interpret a bad measurement, or a profile curve which can be interfered by an unwanted element. This is why some users prefer the direct profile method.

The method by integration consists of making a certain number of consecutive measurements on the same sample, by turning regularly (and always in the same direction) the position of the scanning dial between each measurement.

You must select a sample which contains a good concentration of the elements which you wish to check; a "synthetic" sample, as long as it is homogeneous, can also be used. The same sample must be used for the entire profile operation and we recommend that you always use this same sample for subsequent profiling.

Greasing of the Stand Door's Hinges

Once a month the stand door's hinges and the sample clamp's rod must be greased. Use bearing grease, number AA24714.

Lens Cleaning

We recommend that you clean the lens every six months. In case of very high throughput the frequency could be reduced to two months. When the values of the α standardisation factor of the elements measured in the ultraviolet (<200 nm, for example elements S, P, C, etc.) become high and the instrument is operating in good conditions (vacuum OK), it probably means that the lens needs cleaning; indeed the elements with short wavelengths will most early be affected as they will be absorbed by dirt that lay down on the lens.

There are two types of lenses:

Suprasil used for most of applications without VUV element analysis

CaF_2 used for VUV element analysis

Thermo Fisher Scientific has created à cleaning kit (see catalogue) that is suitable for the two types of lenses.

Use exclusively only the kit provided by Thermo Fisher Scientific for the CaF_2 lens cleaning.

In order to correctly clean the lens, the lens holder must be removed from the stand.

Lens Holder Extraction

The lens holder must never be dismantled. The lens useful area can easily be cleaned without dismantling the lens holder.

Do not touch the lens' fixing screw or of the heating body and never attempt to remove the lens from its holder! Major risks of vacuum leaks and to put optic out or order!

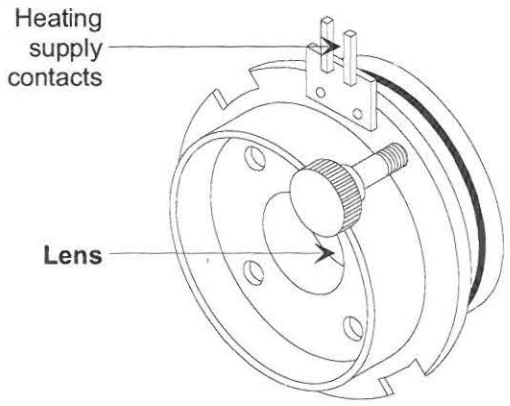


Figure 4.9

Note: To identify the items in the following extraction procedure, please refer to the figures of the *Stand* section of the *Layout and Controls* chapter.

- Open the stand's door, remove the protection plate, turn the manual vacuum shutter completely to the right.
- Remove the analysis table, then remove the primary optical channel taking care to not bend too much the copper pipe attached to the channel. Remove the lens heating connector.
- Slightly untighten the two knurled knobs so as to free the locking clamps. Free the lens holder by screwing a little the extraction screw (red knurled knob).
- Once the lens holder is free, turn it about one eighth of a turn so that the two notches are facing to the clamps. Then take out the lens holder by pulling it towards you.
- Unscrew the red knurled knob so that the extraction screw does not protrude past the lens holder on the side which will rest against the stand's flange. This is important later when the lens holder will need to be set back correctly to its working position.

Note: The lens must be warm, if not contact the local Thermo Fisher Scientific after-sales office.

Proceed to the lens cleaning.

Cleaning

Use exclusively only the kit provided by Thermo Fisher Scientific for the CaF_2 lens cleaning. This kit is also suitable for the Suprasil lens.

The cleaning procedure is as follows:

- Wrap the cleaning stick with paper tissue
- Soak the rolled paper with the ethanol (very pure) supplied in the kit
- Rub lightly the two faces of the lens until stains are removed, repeat these operation 3 times with new paper each time
- Let dry for three minutes before putting back the lens in the stand. The drying time can be reduced by connecting the heating, or by flushing argon

Warning!

Do not clean the lens with the paper soaked in ethanol using your fingers. This risks more dirt on the lens.

Use only the materiel of the kit.

Note: **For the Suprasil lens only (do not apply for the CaF_2 lens):**

If the lens is very dirty, you can proceed prior wit a cleaning for example with iron oxide that is mixed with some alcohol to make a paste, then rinse with alcohol. A good result can also be obtained with toothpaste. It is preferable to use a piece of clean rag or paper (optic paper for example), which does not leave any particles. In order to eliminate particles that remain on the surface, you can blow with argon (never use compressed air that always contains a small quantity of greasy matter). Next finish with a cleaning with the kit, as described above.

Once the lens is clean, do not touch the surface with the fingers any more.

When the lens is dry, put it back by doing the operations in the reverse order. Do not forget to connect the wires on the lens holder contacts.

Note: If, after the lens has been cleaned, the values of the α standardisation factor for elements measured in the ultraviolet have not reduced considerably, the two following conclusions must be considered:

- The lens was very dirty and the cleaning has not been efficient enough; it is imperative to clean it again.
- The lens was clean and the cause of the great α factors must be looked for elsewhere.

Changing or Cleaning of the Dust Filters

At least once a month the dust filters situated at the rear of the instrument should be cleaned. If your environment is very dusty, the filters should be cleaned more often.

For access to the filter, the outside plastic frame must be removed. If you have difficulties to remove the plastic frame, use a screwdriver as shown on the figure below.

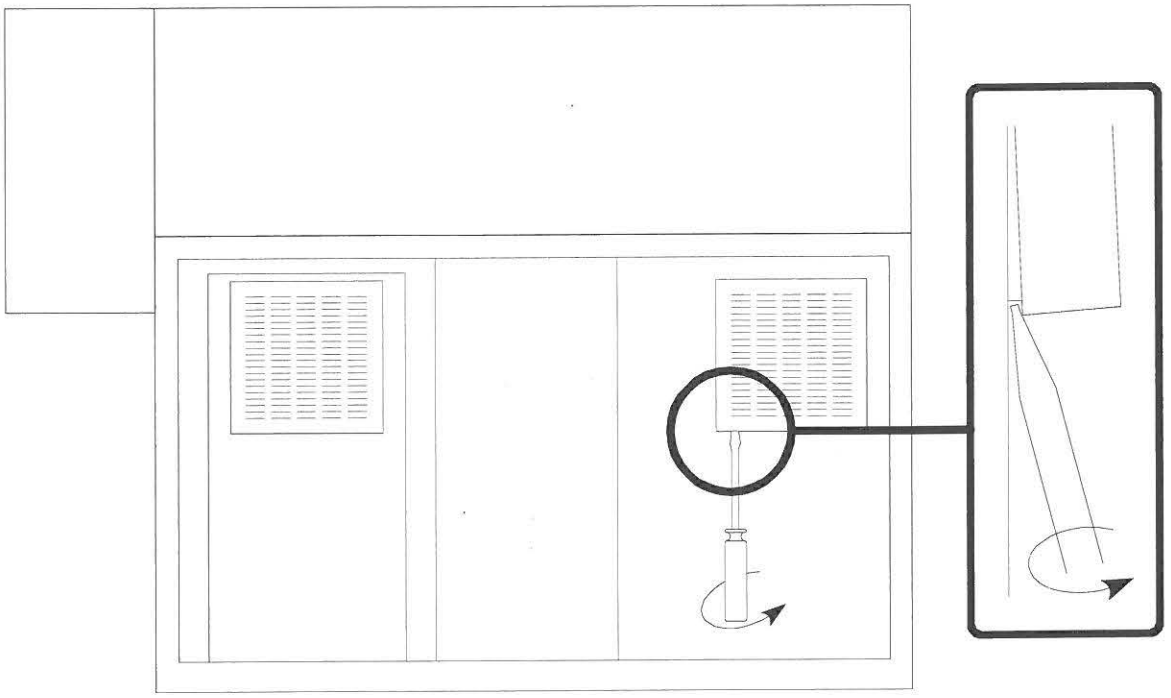


Figure 4.10

In principle, a filter is cleaned with the vacuum cleaner, but it is also possible to wash it in slightly soapy water (in this case, only re-install the filter once it is completely dry).

We recommend you to replace the filters by new ones at least once a year, but more frequently if your environment is dusty. This exchange is automatically done during a service maintenance visit.

Note: The operation of cleaning the filters should not be neglected. A dirty filter becomes too airtight and leads to a temperature rise in the cabinet. This can cause a stability loss in the electronic components, which affects the results. In addition, the most sensitive components can start having discontinued operation (intermittent breakdown), or complete breakdown.

Check of the Cabinet Fans

The control electronics is ventilated from the back by two large fans, one in each bay. The proper operation of these fans must be regularly checked, at least once a week.

To check them, just remove the two front panels of the instrument and observe the operation of the fans. If one is not rotating, contact immediately your local Thermo Fisher Scientific service office.

Analytical Checks

The analytical factor is developed in the *Operator Manual*. Each case is particular, and there are various theories to reach the same goal. If in the past we use to standardise systematically at regular intervals, today the trend is to standardise only when it is necessary.

The use of Control Sample(s), regularly or controlled by computer, helps to determine if it is necessary or not to standardise (partially or totally) the instrument.

Control Sample

The use of Control Sample(s) is optional, but it helps for an efficient use of standardisation. It can be controlled by statistical tools such as the SPC (Statistical Process Control), but it can also be used manually (regularly or randomly).

If this operation is not controlled by the software, we recommend to run at least once a day the Control Sample(s).

The tolerance limits entered in the software (or otherwise the inspection of result deviancy) will determine the need or not to standardise.

Standardisation

When Control Sample(s) does not control the standardisation, we recommend to standardise the instrument at least once a week (at beginning once a day).

The standardisation theory is explained in the *Analytical Principles* appendix on this manual.

Backup

The backup procedure is explained in the OXSAS contextual help.

Backup should be performed at least once a week.

Accessories

Sircal Argon Purifier

In order to keep its efficiency, the molecular sieve must be regularly regenerated. Frequency and procedure are given in the manual supplied with the purifier.

Important:

Before proceeding to the molecular sieve regeneration it is mandatory to remove the argon inlet of the instrument by opening the circuit at the purifier outlet. This is needed in order to avoid impurities and moisture evacuated during the regeneration to enter and pollute the instrument stand.

However, because it is necessary to have an argon flow during the regeneration, you must ensure the purifier argon outlet is not closed by the swaglock fitting, if needed add another fitting with a piece of pipe opened to ambient air.

5

TECHNICAL DESCRIPTION

5 TECHNICAL DESCRIPTION

Function Principle

The ARL 3460 is a simultaneous Quantometer. This means the instrument measures the intensity of several spectral lines simultaneously in the light emitted by the sample, when the atoms that compose it are exited by an external energy source. The analysed light is located approximately into the 130 nm to 800 nm wavelength range.

The whole measuring system is therefore based on the physical phenomenon that is summarised as follows:

When a certain energy is applied to an atom, some of its electrons change their orbit. When these electrons return to their initial orbit, a precise energy is restored in the form of a light at a determined wavelength. This is an atomic phenomenon, and consequently it is practically unaffected by the chemical or crystalline form of the atom. This means the instrument can determine, for example the quantity of silicon in a steel; but will not give information about the form under this silicon is to be found. The figure 5.1 gives a rough representation of this excitation.

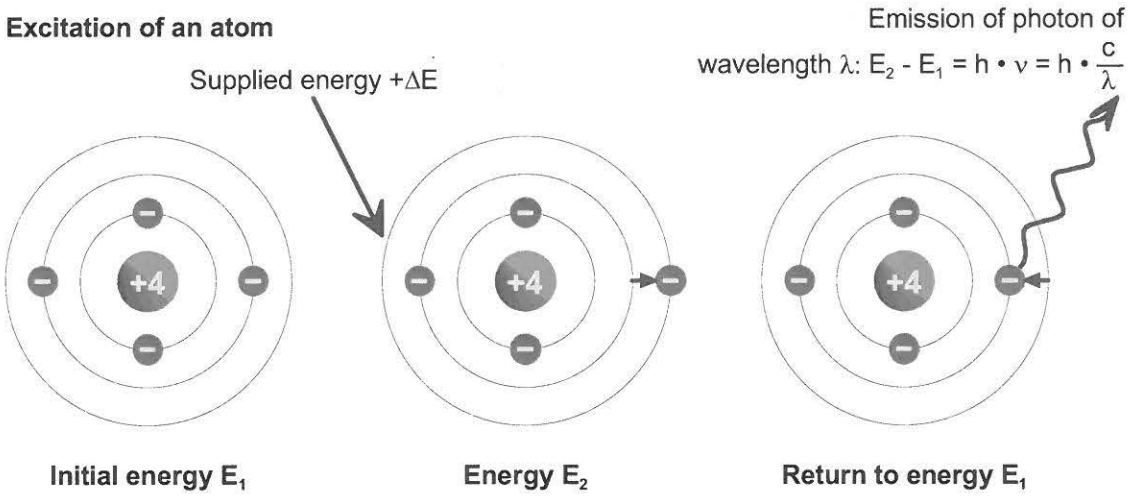


Figure 5.1

A sample containing several different elements will therefore produce light composed of wavelength specific to each of the elements. By separating these wavelengths by a dispersion system, we can determine which elements are present, the intensity of each of these wavelengths being a function of the concentration of the considered element. By measuring this luminous intensity (with a photomultiplier) and by processing this information with a digital analogue converter and a computer, we can thus determine the concentration of the considered element.

An instrument that allows such analysis is therefore composed of the four following parts (figure 5.2):

1) A source of excitation which supplies energy to the samples.

2) A dispersion device which discriminates the different wavelengths.

3) Electronics which measure the luminous intensity of each of the wavelengths.

4) A computer which processes the measurements and controls the instrument.

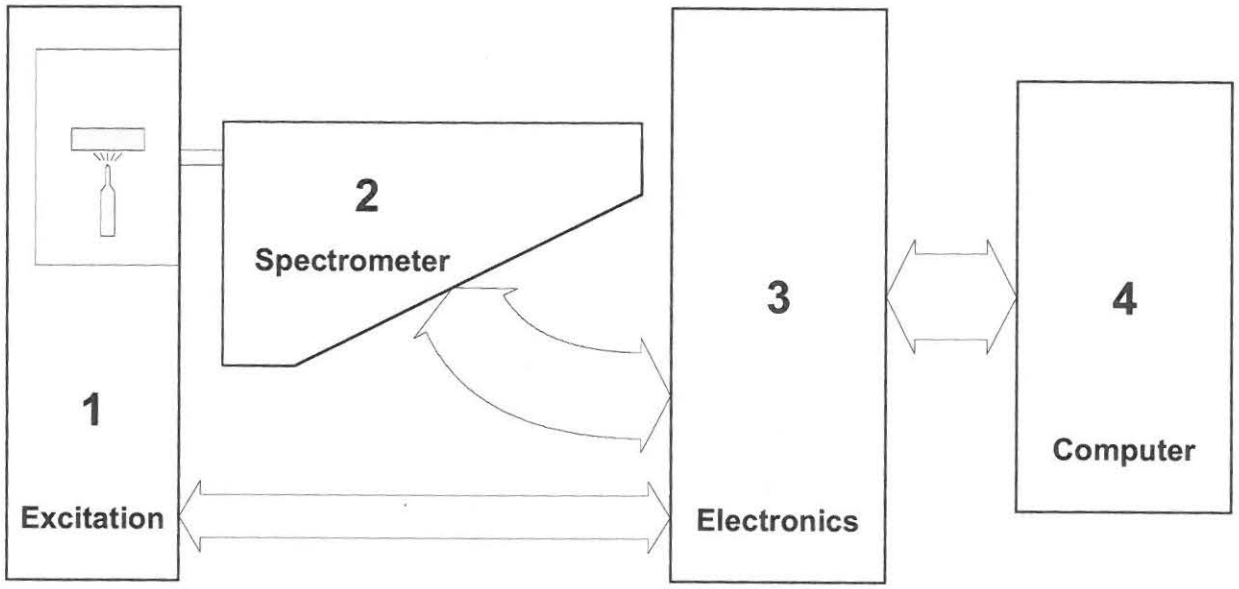


Figure 5.2

Structure of the Instrument

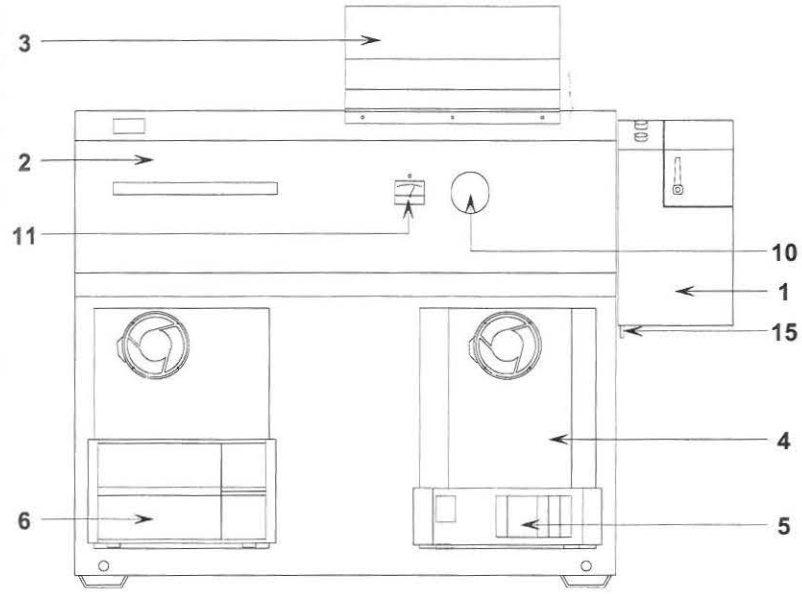


Figure 5.3

1 Stand
2 Oven cover (spectrometer inside)
3 Keyboard support (detachable)
4 230 VAC mains distribution
5 Source
6 Electronic rack
7 Water cooler
8 Argon filter
9 -
10 Access to the scanning screw
11 Multimeter (for vacuum and profile check)

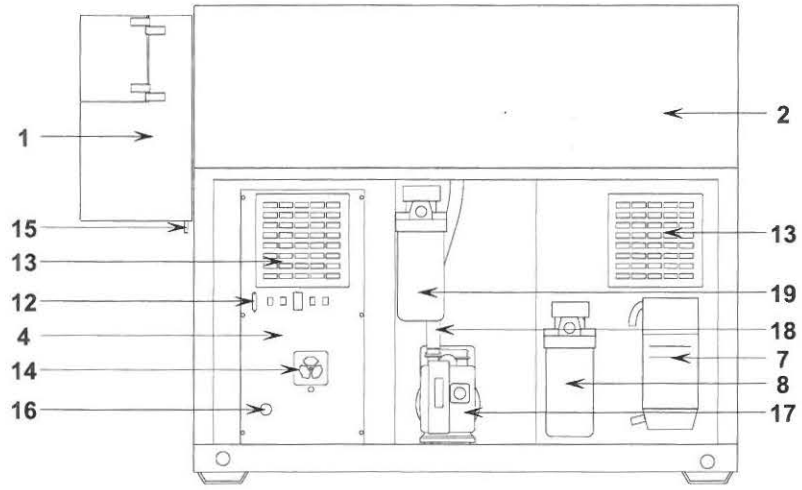


Figure 5.4

12 Input RS232
13 Dust filter (fan inside)
14 230 VAC output sockets (for computer and peripherals)
15 Argon inlet
16 230 VAC mains input
17 Vacuum pump
18 Vacuum pipe
19 Spare filter

Analytical Program and Optical Layout

Each instrument is different to another one, at least by its analytical program (spectral wavelengths installed according to specific application of each customer); the optical layout is a workshop document elaborated on the basis of the analytical program.

The useful information for the operator (analytical program, optical layout, etc.) is to be found in the first pages of the QC/QA/Calibration report, between them:

- The channel number (the same for the attenuator also) and the spectral line used for a chemical element.
- Incidentally, it can also be important to know the sensitivity of the photomultiplier used for this line. This information is shown in the "Pmt" columns of the optical layout. The sign -1 corresponds to the less sensitive photomultiplier and the -3 sign to the most sensitive photomultiplier.
- Depending of the type of grating installed, some of the spectral lines are seen in higher order (order 2, 3, 4). This information is shown in the "A line" column.
- In the case where a line is measured in a higher order, selecting filters are placed in front of the photomultiplier. Those filters are indicated in the "Filt" columns, and the relevant information concerning those filters is shown in the "Interference filter" table of the first page of the optical layout.

The Excitation

The excitation is composed by two distinct parts:

- The source (or generator)
- The stand

The source, called Hi-Rep 2+, is located in the right bay of the instrument (see figure 5.3, position 5). The source is linked to the stand through a high voltage wire and a signal cable. The stand is called MBS201I and contains the igniter of the source, protected inside a Faraday cage.

The Source

The analysis is done by creating a low voltage arc between the surface of the sample to be analysed and a counter electrode. The sparking energy is supplied by a generator called the "SOURCE".

The source into the ARL 3460 is a classical source of the RLC discharge type and its frequency can rise up to 400 Hz. Our Analytical Specialists have looked for the best analytical conditions for each of the material types to be analysed. Our sources are delivered with a certain number of conditions already pre-programmed and optimised for the various matrix required by the customer.

The Stand

The purpose of the stand is to place the sample in a reproducible way relatively to the optical device located into the spectrometer.

The Argon Stand

To avoid any interaction between the air atmosphere and the sample surface, the discharge is made in a sparking chamber under argon atmosphere. The stand therefore constitutes an enclosure in which an argon flow circulates.

The energy dissipated by the sparks heats the sample and the table on which it is placed. The table is cooled by a closed water cooled circuit. This device is composed of a water pump, a tank, and flexible pipes for bringing the cooled water to the analytical table. The separation between the spectrometer under vacuum and the stand under argon is made by an airtight lens, which can be removed for cleaning without breaking the spectrometer vacuum.

During an analysis, two types of sparks are usually created. During a given time, a high energy spark is produced in order to prepare (melt and homogenise) the sample surface. Then a lower energy spark is produced, and the light emitted at this time is measured. In order to avoid the photomultiplier dazzling during the first phase, and also to prevent to make the lens dirty with particles extracted from the sample, a shutter remains closed. This shutter is opened during the measuring phase by an electromagnetic valve.

The argon system that supplies the stand is built so as to allow a small argon flush to circulate permanently around the stand and the sparking chamber, even if the instrument is not running an analysis. The stand-by flow is fixed to about 0.2 - 0.5 l/min. During sparking, this flow is automatically increased. The relation between the stand-by flow and the analytical flow is fixed by restrictors and cannot be altered.

Stand Safety Circuit

The safety circuit protects the operator and the instrument. It is not possible to perform an analysis when the stand door is open. This circuit conforms with the international norm CEI 1010-1.

The Spectrometer

The spectrometer is the mechanical housing that contains the optical dispersion system. The geometry of this system has to be stable in order to guarantee the analytical performances of the instrument. The spectrometer itself is placed into a controlled thermo insulated cabinet called oven (at 38 ± 0.1 °C) in order to avoid any deformation by dilatation. The temperature adjustment is achieved by a heating device whose switching is controlled by a temperature sensor. A certain equilibrium is thus achieved between the heat lost from the enclosure in the ambient air and the heat produced by the heating device.

The light path into the spectrometer is approximately 2 meters long. As air will absorb ultraviolet light, it is necessary to put the spectrometer under vacuum to avoid this effect. The vacuum system is composed of a pumping line, a manual aeration valve for the spectrometer and a vacuum gauge.

For the VUV option, the high vacuum pumping line is composed of a dry membrane pump after which a molecular pump is connected. Such a clean vacuum system allows the vacuum working pressure into the spectrometer to reach 10^{-4} mbar.

In the other case (normal UV only) the pumping line consists of a classical blades vacuum pump. This latter includes an anti suck back device that allows to stop the pump and prevents oil from returning into the spectrometer.

The manual aeration valve is used to fill the spectrometer with air when it must be opened. The Pirani gauge (thermo-couple) permits to measure the vacuum level.

The lens is heated to avoid condensation, and to prevent oil vapour deposit a small air flow is introduced into the spectrometer (the oil vapour particles will be dragged by the air flow and sucked by the pump). This air flow is to be adjusted by a pin-valve in order to keep a vacuum at around 50 µmHg / 0.05 Torr. The pin-valve should be closed when the pump is stopped. With the high vacuum system (VUV option) the air leak must be suppressed by closing permanently the pin-valve.

The optical system is composed of five main parts: the primary slit, the grating, the secondary slits, the mirrors and the photomultipliers.

The primary slit is to be considered as the object in terms of optical geometry, each spectral line is an image of that slit. It has 20 µm width. The grating has a dual feature: it diffracts the light and focuses it on the secondary slits. The grating is a spherical mirror (to focus) marked with extremely thin and narrow grooves (2160, 1080 and 1667 grooves/mm), which does the diffraction.

The secondary slits (around 20 to 150 µm width) constitute the mask that lets only narrow wavelength bands to pass. The slits are fixed to the slit frame holder and an eccentric axle allows to adjust very precisely their position (to ± 2 µm). The light going through the slit is reflected by a mirror that focuses on the photomultiplier.

The photons (light) hit the photomultiplier's photocathode and extract electrons from it. These electrons are captured by the electric field existing between the dynodes of the tube, and then they hit again one of these dynodes, extracting again more electrons. These electron sets are multiplied from dynode to dynode and reach finally the tube's anode. All electron sets reaching the anode constitute the current to be measured. A serial resistor network fixes the potential of each dynode.

The primary slit, the grating and the secondary slits are located on a circle; this is a necessary condition to obtain a proper focus on the secondary slits.

The wavelength crossing each secondary slit depends on the angle formed by the incident beam and the diffracted beam of the grating. The grating curvature is aligned on this circle.

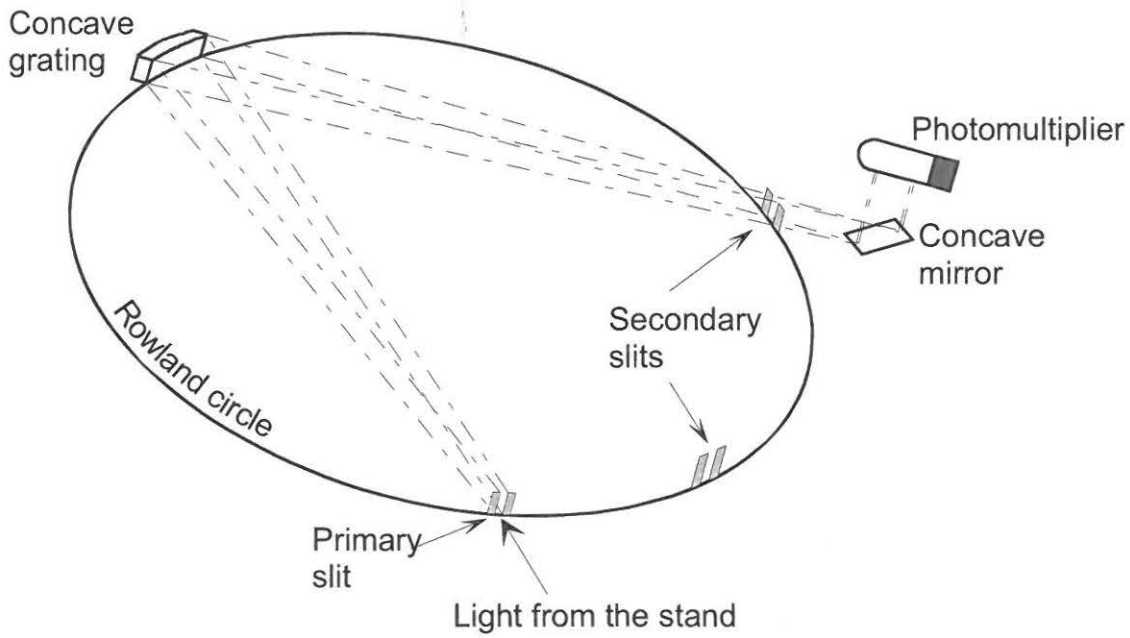


Figure 5.5

By moving the primary slit on the Rowland circle, the wavelength crossing a fixed secondary slit on the circle is modified. This is how the instrument is profiled, i.e. the position of the primary slit is adjusted so that a given wavelength passes through a given secondary slit. This can be achieved, of course, only if relative position between each of the secondary slits is absolutely correct. The primary slit can be manually driven from the exterior of the spectrometer by a micro metrical screw called the "scanning screw".

The Electronic Rack

The electronic rack contains all the necessary circuit for the communication between the computer and the spectrometer. The C-MOS technology is used for the control and interface cards.

The principle is based on control by a microprocessor connected to the main computer. This microprocessor needs an adaptation card to manage the various readout lines, the stand and the source signals.

The low voltage power supplies are produced by two separate modules, one for the +24 VDC, and another one for the +5 VDC and the ±12 VDC.

The rack dimensions are normalised according to the "Europa rack" type. The boards and modules of this rack are:

- The **ICS34B**; this sandwich module contains two boards, the MMB88 microprocessor board, and the adaptation board; this assembly is the brain of the instrument.
- The converter and counter boards for the measure of the signals. One card contains six channels. It is possible to install up to ten IVFC cards.
- The **Vacuum and Profile** board. This board allows the analogue display of the vacuum value or the analogue display of the profile of one channel. Both can be watched on the multimeter on the front of the instrument roof.
- The **Status** board; it allows the reading of a certain number of check points, tied to the good operation of the instrument.
- An optional **Dual Attenuator Control** board can be found too.
- The Low Voltage Power Supplies (**LVPS**) are located at the back of the rack. They power the instrument's electronics, except the excitation (source and stand).
- The High Voltage Power Supply (**HVPS**) is also located at the back of the rack. The photomultipliers are polarised at -100 V and power by -1000 V through attenuator circuits (resistor networks).

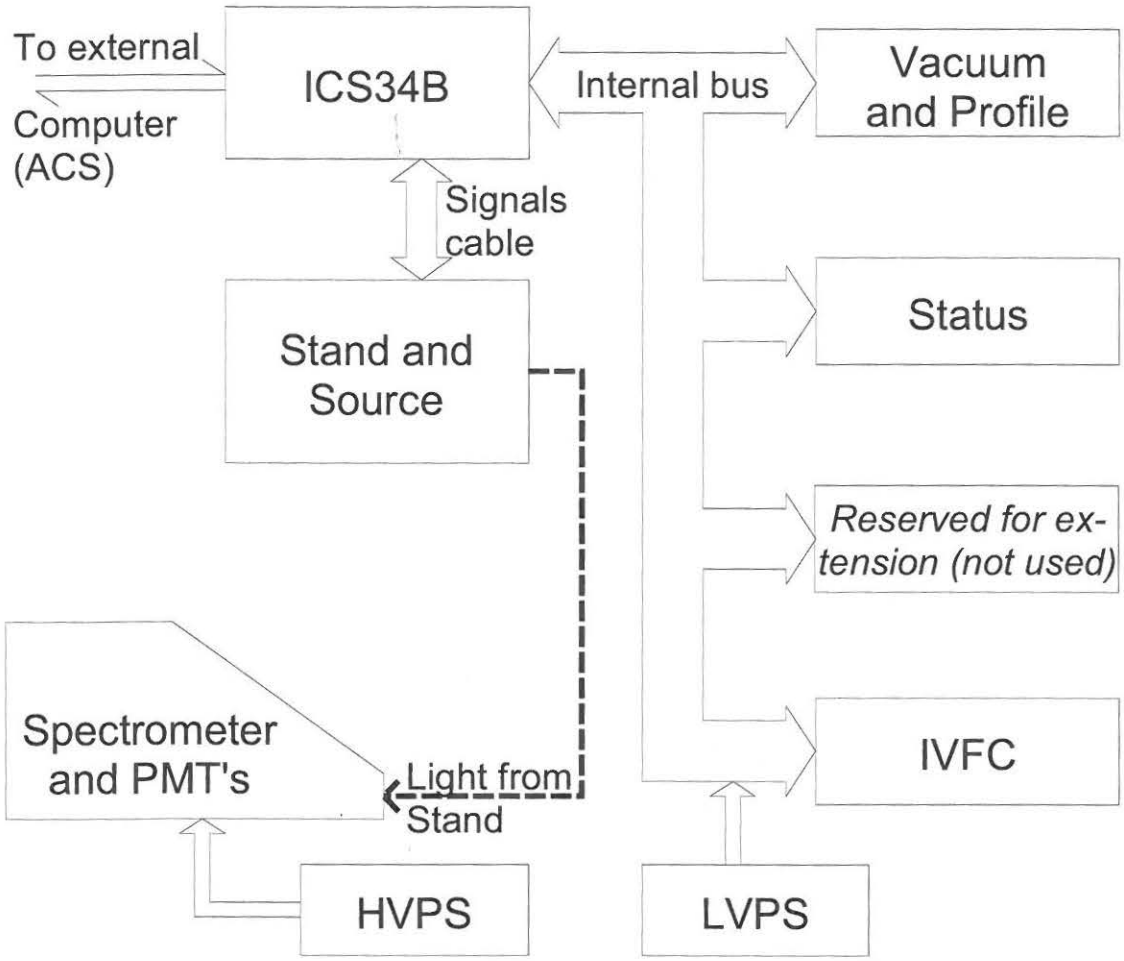

To external
Computer
(ACS)
ICS34B
Internal bus
Vacuum
and Profile
Signals
cable
Stand and
Source
Status
Reserved for ex-
tension (not used)
Spectrometer
and PMT's
Light from
Stand
IVFC
HVPS
LVPS

Figure 5.6

The Computer

The computer fulfils two different tasks:

The instrument control on one end and the calculation of the concentration on the other end.

All data information exchanged between the computer and the instrument is driven on a RS232 serial line type. Data reach directly the instrument's microprocessor that processes it. Analytical results are transmitted from the microprocessor to the computer in the same way.

Computer Configuration

The computer is usually composed by the following main modules:

- the central unit
- the visual display (screen)
- the keyboard
- the mouse

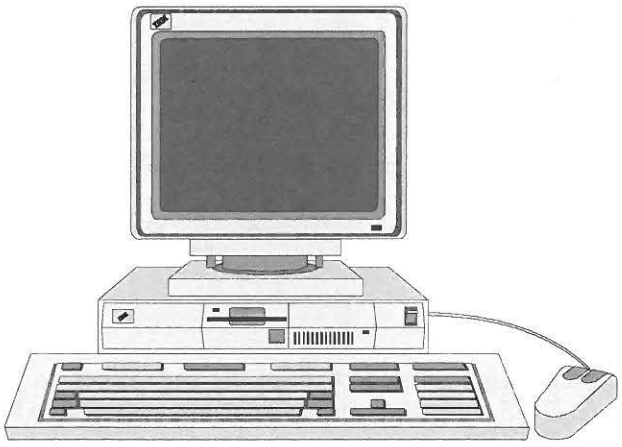


Figure 5.7

A printer is normally connected to the central unit.

Visual Display

The colour screen displays the dialogue between the operator and the computer; the results of the analysis will also be shown on this screen.

Keyboard

The keyboard permits the operator to dialogue with the computer, and to enter the particular data to the application software.

Mouse

Most of software programs are designed to accept command or parameter inputs through a mouse, which can replace a certain number of operations normally done through the keyboard.

Central Unit

The central unit itself is usually composed by the following sub-assemblies:

- the motherboard, including computer system microprocessor (the true brain of the system); the motherboard also contains a part of the memory, interfaces and input/output ports for the screen, the keyboard, the mouse, as well as a serial port (for the instrument) and several USB ports (one for the printer).
- the additional memory of the computer system.
- one hard disk reading unit, and its interface.
- one DVD and CD-ROM reading and writing unit, and its interface.
- additional interfaces can also be found or been added, according to options bought with the equipment (for example for options like COMPAC, NetARL, etc.).

Once the application software is loaded from floppies, it remains permanently into the hard disk; the microprocessor manages and load, if necessary, parts or routines of the application software into the memory.

Printer

Normally a printer is connected on a USB port of the central unit.

The utilisation and routine maintenance of this printer (ribbon or paper exchange, etc.) are explained in the printer operating manual.

Software

The software contains all necessary information to control the instrument, to perform analysis or function tests, as well as to treat results received from the instrument. Options like NetARL, COMPAC, etc., allow to transmit results to other remote units or systems.

If your instrument has been calibrated by ourselves, the installed software will already contain a certain number of data (or parameter) files allowing you to proceed to routine analysis right after the end of the instrument installation. In the other way round, it will be your job to create your own tasks and methods.

The software documentation (and the option's ones if applicable) gives you all necessary information for its loading procedure, its utilisation, and parameter input which will be particular for your tasks.

The Interconnections

The 230 VAC power distribution is summarised on the next figure.

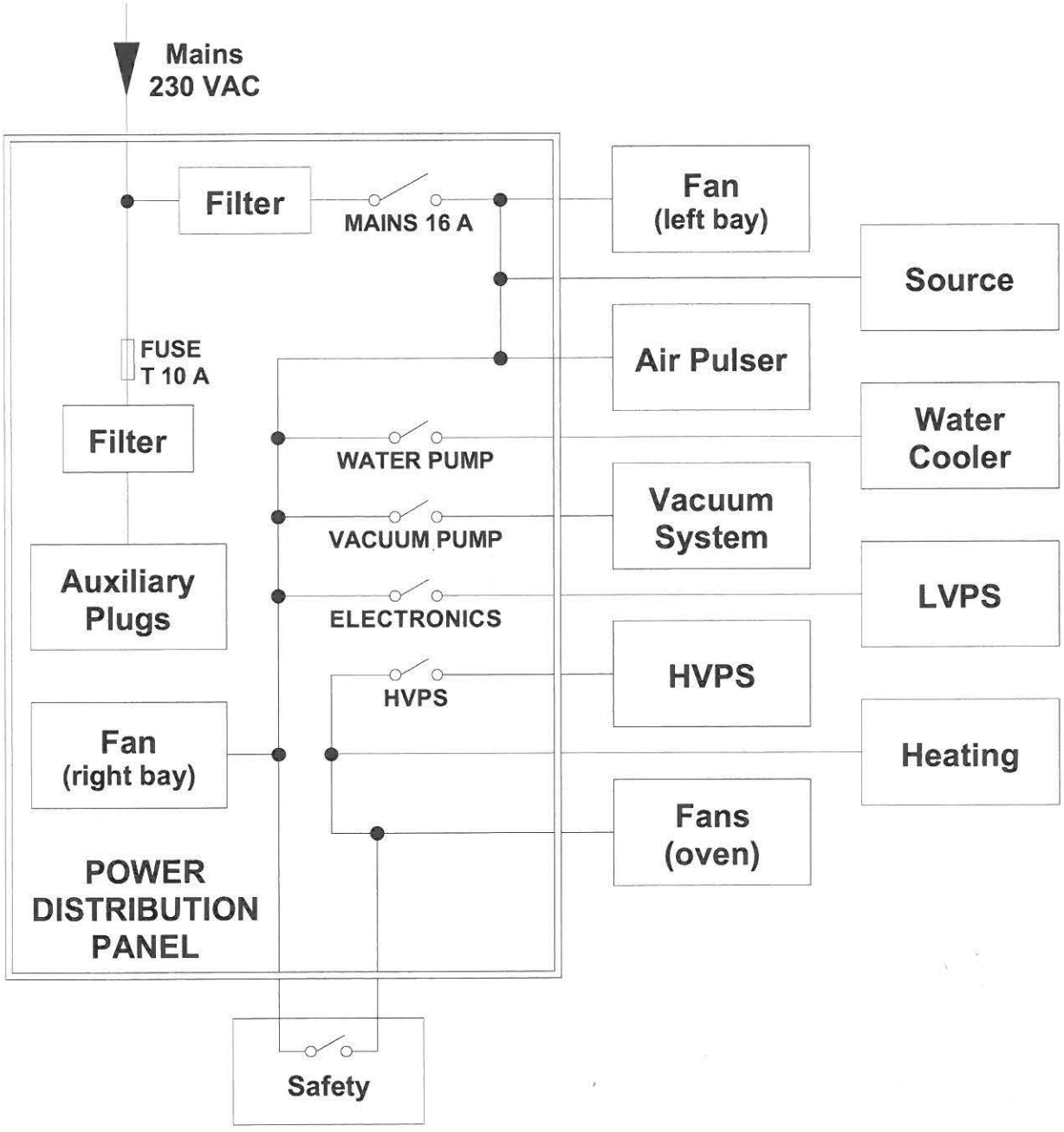


Figure 5.8

By lifting the instrument top roof the safety switches off the photomultiplier's power supply, as well as the heating and fans' power supply. This permits to access the attenuators and other oven items without electrocution risk.

6

ANALYTICAL PRINCIPLES

6 ANALYTICAL PRINCIPLES

Spectroscopy is a comparative method. It is thus necessary to **calibrate** beforehand the instrument for the alloys or qualities that you wish analyse the unknown samples. A brief description of the calibration is described in the section *Calibration.*

The spectrometers are measuring instruments. As the calibration is done once for all and should be valid for the whole life of the instrument, you need to proceed to the **standardisation** operation at regular intervals. The standardisation is necessary to compensate the inevitable internal instrument drifts along the time. The standardisation is part of routine operations and is described in the section *Standardisation (or Recalibration).*

Note: The **standardisation** is also called **recalibration**.

A calibrated instrument whose last standardisation is recent enough is ready to run **routine analyses**. That means to analyses unknown samples and to determine their atomic composition. The routine analysis is described in the section *Routine Analyses.*

Furthermore, in order to keep the optimal instrument performances, a few **routine maintenance** operations are required; these are described in the *Routine Maintenance* chapter. You will find directions for:

- the cleaning of the electrode, the sparking chamber, the stand, the lens,
- the cleaning or exchange of the argon exit filter,
- the cleaning or exchange of the dust filter,
- the vacuum pump oil level check, the change of the oil and gaskets' replacement (if applicable),
- the profile check.

Calibration

In most cases, depending on the contract, your instrument has been calibrated in the factory, or possibly by our engineer after installation.

Forewords

The theory of the calibration belongs to optical emission spectroscopy basics. Depending on the alloys' complexity, a calibration that should guarantee a high accuracy requires excellent analytical knowledge and a strong experience.

The talks in the next section will then only skim over the useful steps for a simple calibration. Before to proceed to the calibration a preliminary step that consists to prepare methods (tasks) must be done with the software. The documentation provided with the software will give you all the necessary information for entering the different data and the processing of the parameters concerning the calibration of your instrument.

Calibration is not part of the installation. If your instrument is not calibrated, or if you desire extensions to the existing calibration, our local representative will be at your disposal to make you an auxiliary offer and to rush you an analytical specialist.

Principle

The calibration consists of measuring standard samples corresponding to different types or alloys whose production will be under your control. These standard samples are normally international certified standard samples – and possibly some of your own production samples as a complement – whose the concentration (the percentage) of most of the elements composing them is known.

We know the result of the measurement of a sample (intensity for each element) by optical emission spectroscopy is proportional to its atomic composition (concentration for each element). This fact is explained in the *Technical Description* chapter.

Thus, for a given element in an alloy or a specific quality, the relation between the concentration in the sample in function of the measured intensity can be represented by a curve, as the example hereunder:

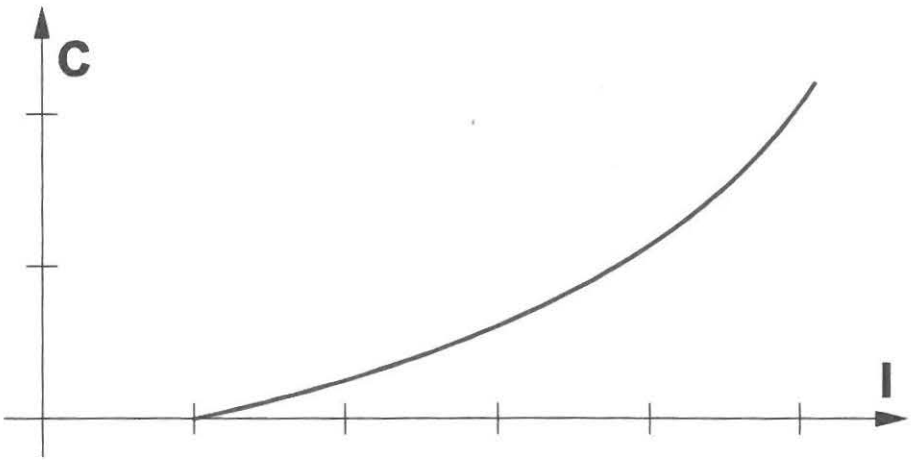


Figure 6.1

By definition a calibration curve is a curve traced by using the measured intensity and the certified concentration of several standard samples.

It is then easy to find the concentration of a present element in an unknown sample, just by reading the concentration corresponding to the intensity on the calibration curve.

In the past the spectroscopist would have to draw families of calibration curves, for all the elements in the alloys or qualities to be measured. Then, after the measurement of an unknown sample, he had to "read" the concentration of those elements on the correct calibration curve (or on tabulations).

Fortunately today those tiresome operations are executed much more quickly and accurately by computerised data processing systems.

The calibration curves are determined and processed by the operation called the **regression calculation**. This operation consists to find the coefficients of a polynom, whose the equation is the closest mathematical image of the calibration curve. The analytical software is able to calculate regression for polynoms of the first, second and third degree. The mathematical equation that summarises the relation of the concentration (**C**) in function of the intensity (**I**) is of the following type:

$$\mathbf{C\ [\%] = A_0 + A_1 \times I + A_2 \times I^2 + A_3 \times I^3}$$

A_0, A_1, A_2 and A_3 are the polynom coefficients, and are stored by the software. If the polynom is of the second degree A_3 is nil; and if the polynom is of the first degree (straight) A_2 and A_3 are nil.

The coefficients for each curve are stored in a software file. Like this, when an unknown sample is measured, the software is able to find the concentration of the element composing the sample by applying the polynom's formulas on the measured intensities.

Complexity

Unfortunately the calibration operation is not as simple as described in the above section. The chemical and physical behaviours of the samples' metallurgy are making the life of the spectroscopist more difficult.

Without speaking of details, the chemical behaviours are usually bound to problems concerning the crystalline state of the sample; we speak here about inter-element effects. The problems of the physical behaviours are themselves bound the limits of the dispersion device (spectrometer, see *Technical Description* chapter); we speak here rather about interference.

If inter-element or interference effects are not taken into account, the points of the calibration curve for one or another element can be dispersed. Sometimes they can be so much dispersed that drawing (calculating) a curve is even impossible. When the major effects are not properly corrected, the results of the analyses are inaccurate, if not often unreliable!

The analytical software has the capability to correct those phenomena by using mathematical additive or multiplicative corrections routines.

Determining the additive and multiplicative correction factors is not an easy task! This requires advanced emission spectroscopy knowledge, and usually several years of practice.

Note: Since already several years, Thermo Fisher Scientific has set-up an outstanding system called **CARL** (**C**alibration **ARL**) used to calibrate the instruments directly in our factory. Data of this system are regularly updated, and we own know a database collected on thousands calibrated instruments. This is why we can only recommend our customers to benefit from our experience and to let us calibrate the instruments.

Summary

The following steps necessary to calibrate one or several qualities or alloys on an instrument are summarised hereunder:

❶ Instrument under voltage ready to be used, and in a stable state (see *Routine Operation* chapter).

❷ Preparation of the analytical task; that means entering data and parameters into the software (see software documentation), choice of standard and setting-up samples according to the applications.

❸ Routine maintenance operations check (see *Routine Maintenance* chapter).

❹ Sample's surface preparation for the samples needed to accomplish the task; that is the certified standard samples and the setting-up samples (see *Sample Preparation* appendix).

❺ Initial standardisation (see section *Initial Standardisation* of that manual).

❻ Analyses in intensity of standard samples. If the task is large (i.e. it takes a long time to perform the job), it will be necessary to proceed to intermediate standardisations in-between the standard samples' analyses!

❼ Regression calculations, that means determining the working calibration curves' polynom coefficients.

❽ Determining the interelement or interference correction factors.

❾ Correction or review of the concerned regression calculation.

Standardisation (or Recalibration)

The purpose of the standardisation is to correct the instrumental drift at the medium and long term. The instrumental drift is due to several causes such as:

- ageing of some of the generator electrical components that influences the sparking energy,
- photomultipliers' ageing,
- dirt on some optical components, such as the lens.

The drift will be influenced by the sample throughput.

The standardisation is considered as a routine maintenance operation. It is essential and guarantees reliable accurate results all along the instrument's life.

Principle

Experience has shown that instrumental drift is practically linear; so much so that in principle the application of a correction by a first degree equation (rotation and translation) is sufficient for the correction.

The standardisation principle is very simple:

For each element measured, two reference "points" are required; one situated in the low part and the other in the high part or the working curve. Therefore two samples are needed, not necessarily (expensive) certified standards whose element concentrations are precisely known, but **setting-up standards** (SUS) whose homogeneity is recognised in the whole volume of the sample.

The "low point" is often represented by a so-called "pure" sample, meaning that it contains practically only the matrix (or the base) of the alloy; for example a sample of pure iron. Apart from the matrix element, the composition of the other elements should be nil, insignificant or minimum.

The "high point" is represented by a sample containing a high content in concentration of the element(s) that are present in the alloy to be measured.

Theoretically, two samples are thus sufficient to standardise the instrument; however in practice it is difficult to find one only "high point" that is suitable for all the elements. It is therefore often necessary to have three setting-up samples or more to cover the range of concentration of all the elements. The standardisation applies to one ore more alloy families. All the setting-up standards (low points and high points) which are necessary for the standardisation of an alloy (or a group of alloys) must have been measured at the same time as the standard samples which are necessary for the calibration – in fact just before, during the initial standardisation, see the section *Initial Standardisation* hereunder.

After a certain time (that can be set by the software) during routine analyses, an alarm message will be displayed on the screen, informing that the instrumental drift should be compensated. The operator will then proceed to the standardisation update procedure.

Drift Correction Equation

Since it is admitted the drift correction is linear, the equation is of the type:

$I_{nom} = \beta + (I_{mes} \times \alpha)$ where:

I_{nom}: Nominal intensity (during the initial standardisation),
I_{mes}: Measured intensity (current),
α: Slope correction factor (multiplicative),
β: Translation correction factor (additive).

After all the setting-up samples have been run, the system stores for each of the elements the – current – intensities just yet measured (I_{mes}). Then, those intensities are compared with the ones stored when these same setting-up samples where run during the initial standardisation (I_{nom}).

The software calculates – from measured and nominal intensities of low and high setting-up samples – and displays then automatically the drift correction factors for all the concerned elements.

Later on – during the routine analysis of any sample – the drift correction equation will be applied to the measured intensity for all the elements. That correction will bring back the measured intensity to the nominal one, allowing to determine the concentration of the element on the calibration curve.

Recommendations

The observation and the regular comparison of the correction factors α and β will give you an idea of the stability of your instrument. β is a small positive or negative figure close to 0 (zero), α is a positive figure fluctuating around 1 (one). Large variations between two standardisations (especially for α) can give you an indication that there could be some problems at the instrumental response level. We recommend you to print out factors α and β after a standardisation and to keep these papers. They could be very useful to the service engineer during a service.

If the progression of factor α is regular and slow, even a considerable variation (0.5 or 2) in comparison to the initial value (of 1) can be accepted and corrected properly by the software. However, a big α correction factor for the elements analysed in the ultraviolet (for example Phosphorous, Sulphur, etc.) probably indicates exaggerated soiling of the primary lens, which needs to be cleaned, or a pressure increase into the spectrometer tank.

Standardisation update is the last routine maintenance operation to be done before the analysis of unknown samples. We mean by this that the other maintenance operations (profile check, lens cleaning or sparking chamber cleaning, etc.) must always be carried out before proceeding with a standardisation. In the case where you decide nevertheless to carry out maintenance operations "between two standardisations", we strongly recommend you to proceed with a standardisation immediately after the maintenance carried out if you then wish to analyse unknown samples. It is in fact that the maintenance operations can strongly affect the instrument's response, and thus, in the absence of a recent standardisation update after maintenance, falsify the results.

Frequency of the Standardisation Cycle

The stability of the instrument, by comparing the values of the drift correction factors, will allow you to decide the frequency of the standardisation update cycle. A high analyses' throughput will force you to standardise more frequently in order to guarantee the precision of the results.

The frequency of standardisation is thus a choice of the user, in accordance with the desired precision and the confidence in the instrument's stability.

In the beginning, for lack of values observed over a long period, we recommend standardisation at each shift change, or at least daily, in the morning at the beginning of the working day.

Under some conditions (air-conditioned laboratory under a correct pressure and temperature control, with stabilised mains, and a relatively low sample throughput) the standardisation cycle can be extended up to several days.

Remark:	The frequency of the standardisation cycle can be optimised and driven by the optional SPC software (SPC = Statistical Process Control).

Procedure

The software documentation explains the standardisation procedure. The operation progress depends on various users selectable criterion.

The setting-up samples that are necessary for the calibrated methods delivered are provided with the instrument.

Initial Standardisation

Before calibrating a group of qualities or alloys, it is necessary to proceed to the operation called **standardisation initialisation**.

The initial standardisation has the goal to store once for all the nominal intensities (I_{nom}, see section *Drift Correction Equation* above) of the low and high setting-up samples. These initial values will be used as reference for calculating the α and β correction factors after the later standardisations.

The selection of some criterion or parameters must first be done. This choice, as well as a procedure and its progress is explained in the software documentation.

Replacement of the Standardisation Samples

As they are used very frequently, the setting-up samples will eventually become unusable because they have been worn too thin. Thermo Fisher Scientific can deliver equivalent samples so long as they are still available on the market. However, an equivalent sample will never have concentrations that are identical to those of the substituted sample, and thus will not have an identical intensity response for all the elements.

The procedure principle to be followed for the replacement of setting-up samples is as follows:

- ⇨ Carry out a standardisation with the "old" setting-up samples. **This must of course be done before the samples become unusable!**
- ⇨ Analyse the "new" setting-up samples, in intensities corrected by the drift. These intensities thus correspond to the nominal intensity of the new samples (as if the samples had been analysed during the initial standardisation, just before the calibration).
- ⇨ Modify in the software's corresponding files, the nominal intensities of the appropriate elements; therefore by entering these new nominal values.
- ⇨ Carry out another standardisation using the "new" setting-up samples this time. Check the validity of the last standardisation.
- ⇨ Do not forget to make a backup of the files.
- ⇨ The instrument is now ready again to go on with routine analyses.

A detailed procedure can be found in the software documentation. By following scrupulously that procedure, it is not necessary to modify manually the intensities into the files, the software will do it automatically.

ATTENTION, IMPORTANT!

The operations described above must be done with the greatest care. This is because the accuracy of all the following analyses depends upon them. We recommend that you analyse each sample at least five times and that you carefully study the results displayed for the choice of the average; we also recommend that you display the relative standard deviations (σ%) of theses analyses so as to check the reproducibility. In case of problems or doubts, do not hesitate to consult the local Thermo Fisher Scientific representative for advice.

In the case where the "new" setting-up samples available on the market are no longer equivalent to the "old" ones (different distribution of concentrations and elements in the samples), the replacement principle for these samples remains the same. However you will have to modify not only the nominal intensities in the corresponding files, but also to modify slightly the structure of these files so that they correspond to the new distribution of the elements and concentrations in the new setting-up samples. Here too, our analytical specialists or our service engineers can advise you.

Routine Analyses

Routine analysis consists of measuring an unknown sample in order to determine the concentrations of the elements that are composing it.

You can thus analyse any random sample, as long as its composition is compatible to the method or the calibrated alloy that you are going to use in the software.

General

The sample must be "prepared", that is to say it must have a surface that is clean, smooth and flat and at least slightly bigger than the hole of the analytical table. The accuracy and the precision of the analyses mainly depend on the state of preparation of the surface to be analysed. The sample preparation is explained in the *Sample Preparation* appendix.

The prepared sample is placed on the stand's analytical table, then the stand's door must be closed. How to place the sample on the table is explained in the *Routine Operation* chapter.

The analysis is started by a software command, using the mouse (or the keyboard). The measurement cycle itself must be activated by pressing the green button (START) on the stand.

Note: This last action can be automatic (automatic start mode) and because of this the operator does not need to press the START button on the stand. In such a case, the cycle starts as soon as the stand's door is closed (and all safeties are OK). Concerning the automatic start mode, refer to the software documentation.

At the end of the measurement, the results are displayed on the screen. The operator can choose to run a new measure, to perform the mathematical average, or to quit the routine.

One measurement can be sufficient to determine the concentration of the elements that are present in the sample. However we recommend that you take several measurements so as to guarantee a greater result precision. In the same way, the production control samples are often imperfect (they contain inclusions, or are not very homogeneous). Taking several measurements and selecting the mean (or making the software do it) rejects any doubtful results of a sparking on an inclusion or handling error – or sampling position error – by the operator.

Here again, the choice of the number of measurements to be done for the analysis of a sample is up to the user. Nevertheless the experience has shown us that 2 or 3 measurements are usually enough in case of homogeneous samples correctly prepared.

Measurement Cycle

The measurement cycle is generally the following:

⇨ **Start-up** by pressing the green START button.

⇨ **Flushing** of the sparking chamber, generally 3 seconds.

⇨ **Pre-integration** period, with reinforced discharge condition, necessary for the homogenisation of the sample's surface to be measured, usually from 7 to 12 seconds (longer for grey cast iron alloys or free cutting steels).

⇨ **Integration** period, with normal discharge condition, during which the current – proportional to the luminous intensity received by the intermediary of the dispersion optic system – emitted by each photomultiplier will load the electronic counters corresponding to the channels (elements), usually 3.5 seconds.

⇨ **Readout** of the counters (acquisition of the measurements), usually several milliseconds.

⇨ **Processing** of the measurements (conversion in concentrations, correction calculations, iterations, etc.) by the software, usually several milliseconds.

⇨ **Display** of the results, usually several milliseconds on the screen to several seconds on the printer (depending upon the type).

The sequences of integration, of readout and of processing, can be repeated automatically, if the multi-integration parameters have been programmed (different sparking conditions for different elements).

Prevention or Cancellation of a Measurement

A measurement cannot be taken if the stand's door is open, or if one of the other conditions of the analysis safety circuit is not fulfilled. In such a case, a message for the operator is displayed on the screen.

A measurement can be interrupted by the operator at any time, either by opening the stand's door, by pressing the stand's red emergency STOP button, or even by using the mouse on the **Abort** or **Stop** command button on the window. It can also stop by itself, if during a measurement cycle, one of the analysis safety circuit conditions is not fulfilled. A message for the operator is also displayed on the screen in these cases.

Analysis Cycle

The analysis cycle is nothing more than the start-up of the measurement cycle and its repetition as many times as we require the same sample to be measured; then finally to choose the mean of the measurements so as to obtain the final analysis result.

Thus to resume:

① Start-up of the software's analysis routine, answer questions asked by the software (method choice, sample identity, etc.).

② Placing the sample on the analysis table, closing the door.

③ Start-up of the measurement by pressing the START button on the stand's housing.

Remark:	The analysis may start as soon as the stand's door is closed, without waiting the START button to be pressed, if the automatic start mode is selected.

④ Waiting until the end of the measurement cycle, and observation of the displayed results. Usually decision to run one or two more measurements (back to point 2), otherwise go to point 5.

⑤ Measurements' selection for the average calculation.

Remark:	This selection can be done automatically by the software, according to user selected decision's criterion.

⑥ End of analysis; the instrument is ready for the analysis of another unknown sample.

Remark:	Without to quit the analysis routine, the software let you to select other kind of tasks or methods for the analysis of other alloy types.

A

SAMPLE PREPARATION

A SAMPLE PREPARATION

A suitable sample taking and a careful surface preparation are absolutely essential. Indeed, it is necessary to have a sample as homogeneous as possible without inclusions on one hand, and on the other hand a clean and flat surface is needed in order to insure reliable and reproducible measurements.

For the sample taking, several kinds of moulds can be bought or machined. As well for sample surface preparation, several kinds of machines that are suitable exist on the market.

Your local representative will gladly advise you about the type and model that will fit at best for your own application. We remember hereunder only general aspects of the various sample preparation machine types and their main applications.

The section *Sample Taking - Moulds* points out a few mould types for the sample taking.

The section *Surface Preparation - Sample Preparation Machines* points out a few machine types for the sample's analysis surface preparation.

Sample Taking - Moulds

The sample taking for spectroscopy analysis is a fundamental step. Several spectroscopy books explain that stage and advise suitably about the mould's choice for a given application. ISO and ASTM standards also provide specifications and information about that subject.

Usually:
- ⇨ The sample cooling must be quick so that a fine grain metallic structure is kept.
- ⇨ The mould will be in copper and maintained clean.
- ⇨ The mould in stand-by of use must be turned upside down (or covered) in order to avoid dirties or other material to be introduced into it.

Here are some examples of moulds that are suitable for casting good quality samples and adapted for optical emission spectroscopy analysis. A probe for direct sample taking is also shown.

Non Ferrous Metals

The mushroom form sample taking is the most used for non ferrous metals. There are however segregation risks, and the mould diameter must be adapted.

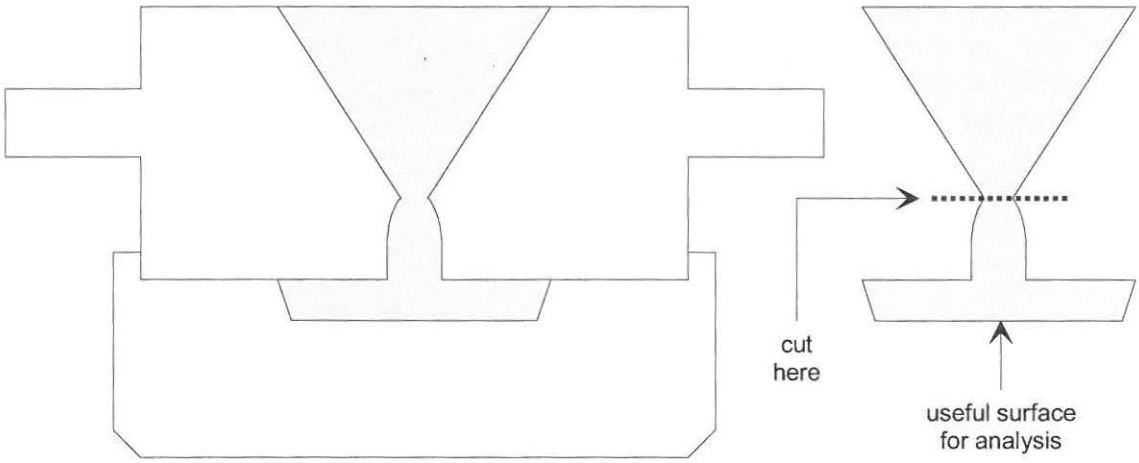


Figure A.1

Fe, Ni, Co Bases

Here is a very simple mould, frequently used for alloys of Fe, Ni and Co bases. (More specifically for cast irons and traces, see hereunder sections *Cast Irons* and *Traces*)

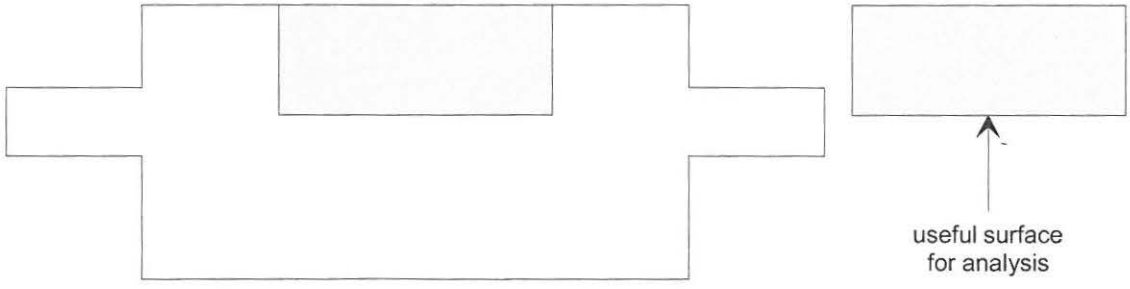


Figure A.2

Cast Irons

The kind of mould hereunder is specifically adapted for casting cast irons in general, and pig iron in particular. The cooling speed is very high.

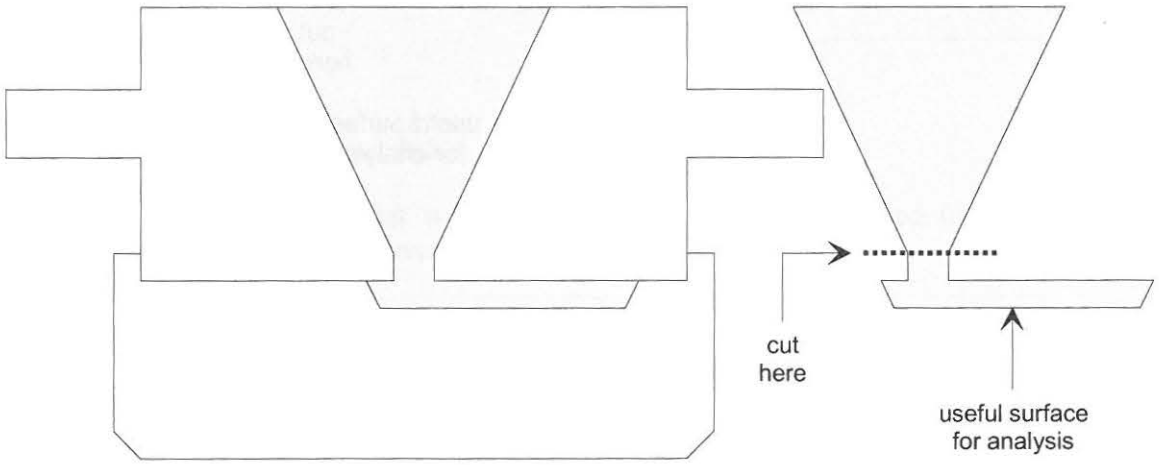


Figure A.3

Traces

The ring mould type, as shown hereunder, is advisable for casting pure metals (traces' analysis), or metals that will have low tendency to segregation. The ring is of stainless steel or ceramic, so that the sample will be mostly cooled by the bottom copper plate. **The sample is homogeneous on its surface, but only on some few millimetres in depth!**

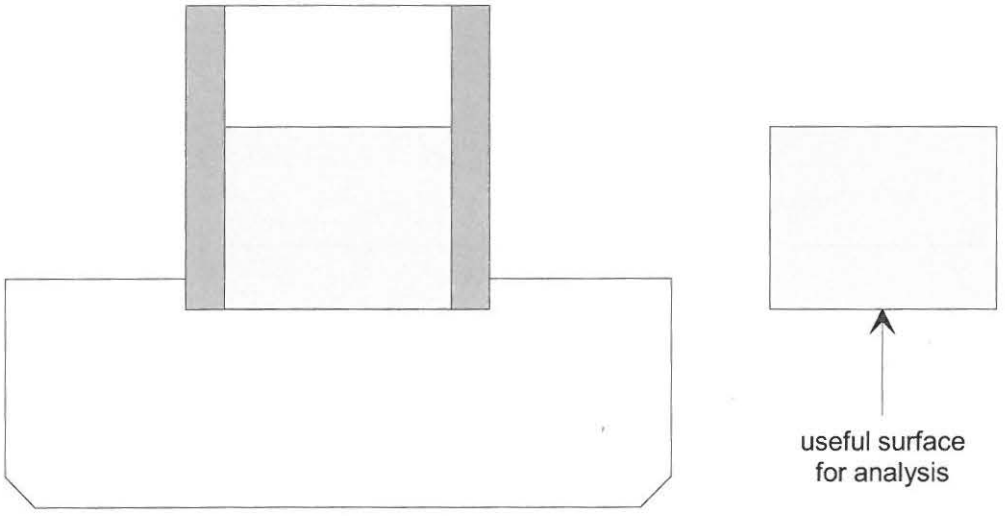


Figure A.4

SPEMIS Probe

For steels, the sample taking can be greatly simplified with a **SPEMIS** probe that can take liquid metal directly from the casting. The sample obtained has the following form:

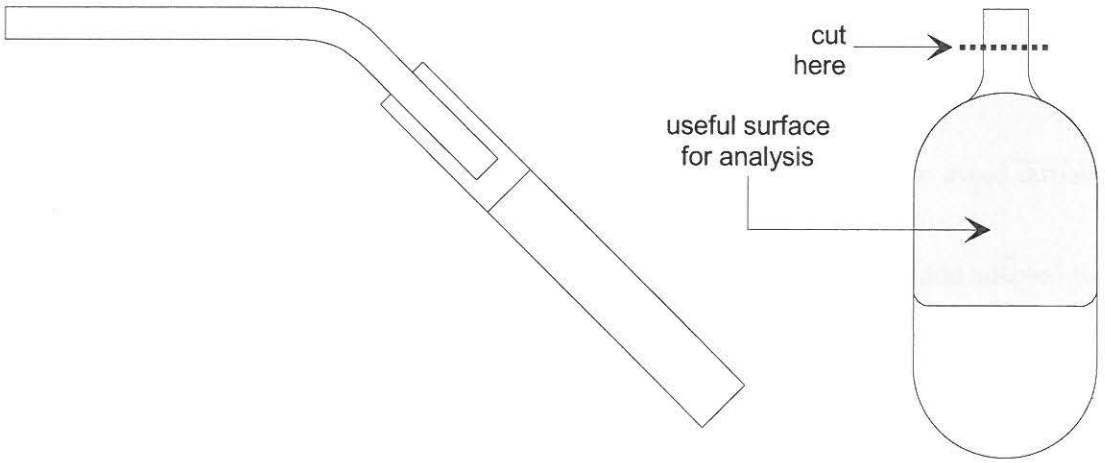


Figure A.5

Surface Preparation - Sample Preparation Machines

It is essential to use an appropriate machine in order to obtain a clean and flat surface. We recommend the use of one of the following sample preparation machine types:

Disk Sander

This is a sander with a rotary abrasive disk.

Some machines have two disks; that is convenient if a coarse grain is used for preliminary surface preparation, and a fine grain for final preparation.

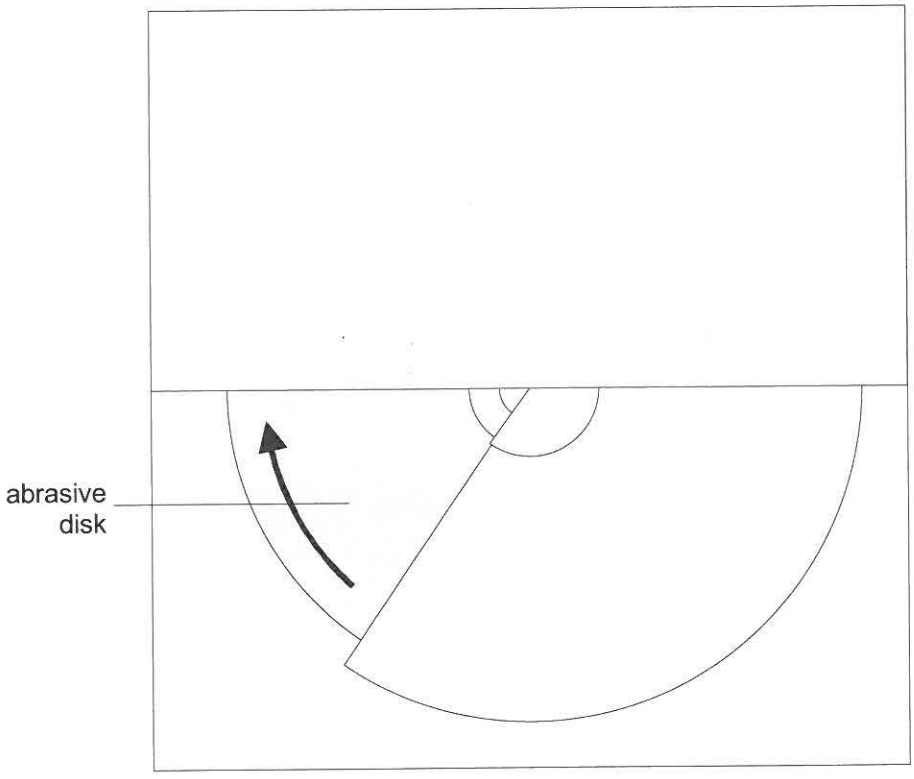


Figure A.6

This surface preparation method is the quickest way to prepare **iron**, **nickel** and **cobalt** samples (as well as some few coppers). Sample must be thick enough so that they can be hold with fingers without the risk to injury themselves.

The abrasive paper may always distort the result of some analyses, especially for elements in low concentration in the sample. The choice of the paper depends on which elements must be determined or not. The abrasive paper disk based with aluminium and silicon oxide mixed with resin (Al/Si = 1.47) is usually suitable. A grain of "80" or "60" is recommended. If this paper seems to distort the result on some elements, try another one that does not content the distorted elements. In case of doubt consult our local service for advice.

Note:	The metals like copper, aluminium, lead, zinc, magnesium, etc., pure or even very low alloyed, and generally all soft material, cannot be properly prepared on abrasive paper disks.

Surface Grinder

Rotating surface grinders with multiple grindstones fixed on a rotating arm are recommended, as on the example shown hereunder:

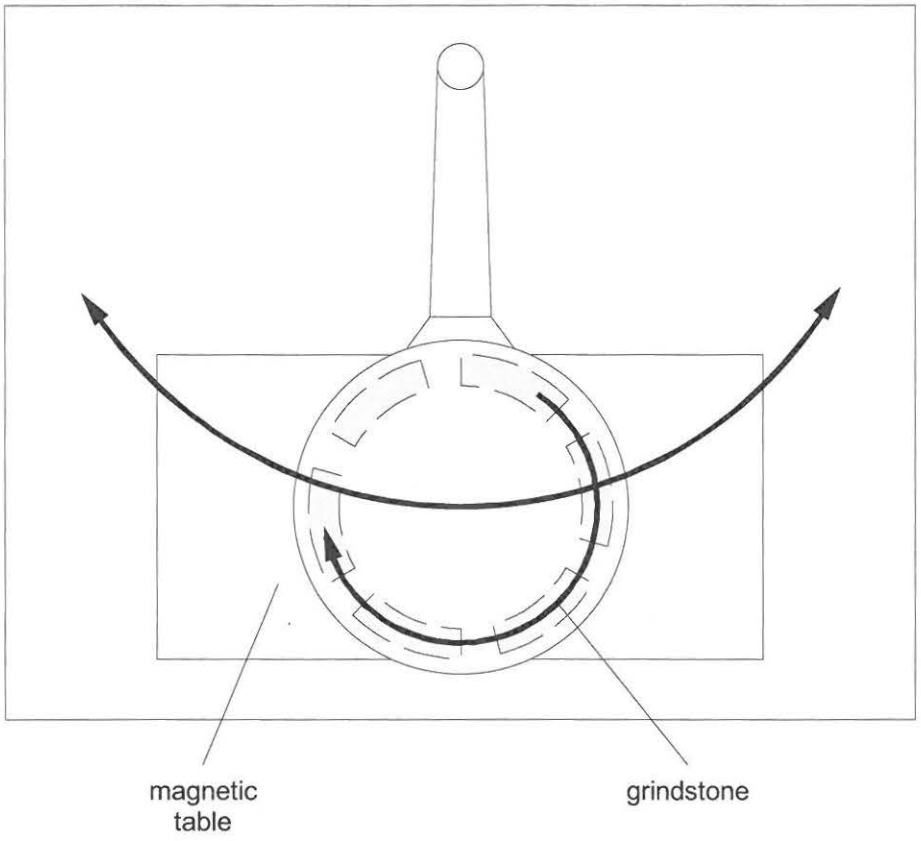


Figure A.7

This method is suitable for all sample kinds of **steels** and **cast irons**, as well as for **nickel** and **cobalt** alloys.

No cooling liquid must be used.

The magnetic samples will be kept still by the magnetic table. The non-magnetic samples must be fixed on a magnetic vice.

The grindstones must be regularly sharpened, otherwise the risk of surface overheat and deterioration of the sample is high. This can be the cause of bad sparking spots.

Milling Machine or Lathe

Such a machine should be equipped with a milling cutter or chisel of tungsten carbide.

The milling machine is the ideal machine for preparing all **aluminium** alloys, as well as **pure coppers** and other **soft metals**. The milling is also the recommended method for the sample preparation of steel analysis with nitrogen and carbon at lower than the 10 ppm level, or inclusions analysis.

For the analysis of oxygen, milling is mandatory to limit surface contamination (CNO option).

The milling machine is more suitable than a lathe for sample with complex shapes, for example melted or machined pieces. Moreover, the cutting speed is constant with the milling machine, that insures a regular machined surface.

The surface preparation is normally done without coolant (i.e. dry). However – for aluminium samples – a little of isopropyl alcohol can be used. Oil or any other coolant must be prohibited. The head and the table of the milling machine, the milling cutter, the vice for holding the sample, must be cleaned before the use for sample surface preparation if the machine is used for other means that requires oil, water, or another coolant.

As for example, some steel springs can be analysed if prepared like the following picture represents it (surface preparation by milling or polishing):

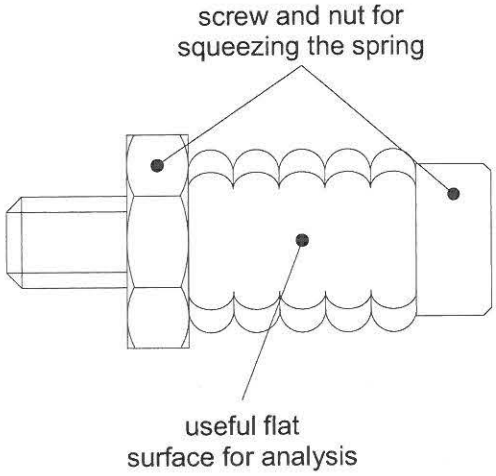


Figure A.8

Press Machine

For soft wire sample, one can flatten them with a pressure among 20 to 40 tons with a press.

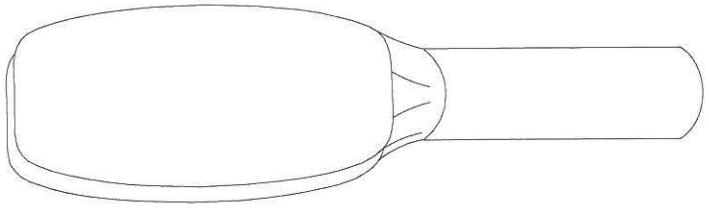


Figure A.9

If the useful surface to be analysed is smaller than the 15 mm standard hole of the carbide tungsten disk, one should use another disk, that is equipped with a smaller hole.

Inductive Furnace

Metallic chips can be re-melted in a fusion furnace. This furnace provides solid samples that can be used for spectroscopy analysis.

B

SPECIAL PROCEDURES

B SPECIAL PROCEDURES

This appendix brings together the particular routine maintenance procedures required for the analysis of some alloys, in relation to the ordinary routine maintenance procedures described in the *Routine Maintenance* chapter of this manual.

This concerns:

- **Magnesium Alloy Matrix**

For all matter not explicitly described in this appendix, refer to the procedures described in the *Routine Maintenance* chapter.

Magnesium Alloy Matrix

General Consideration

The analysis of magnesium samples by sparking produces inevitably magnesium powder. This magnesium powder has a chemical property to catch fire or at least to make sparkles when oxidising (in contact with the air). In an airtight environment a sudden air entrance may even generate a small explosion. If the oxidation is slow, these effects are greatly reduced.

It is thus necessary to act with prudence with the maintenance of the parts likely to store magnesium.

Working Constraints

A special argon filtering device must be used on the exhaust. In the case of a multi bases instrument with the Mg base, a commutation valve is inserted in order to reroute the argon exhaust either on the special Mg filter kit or to the traditional argon filtering system. Waiting time constraints tied to the commutation between the devices are to be considered too. The *Mg Filter Kit* manual relating safety instructions, and the maintenance of the filtering device is supplied with the instrument and must imperatively be read. The procedures inside this manual must be applied in order to ensure the safety of the personal.

The use of single tip electrode, to prevent from mounting it in the inverse direction, and consequently to prevent from confining an eventual magnesium deposit into the cavity under the electrode holder cylinder.

Particular Equipment and Tools

The use of acid being recommended for the cleaning of some hardware, the availability of a chemistry laboratory or at least a working place under a ventilated vault is necessary.

Because of the risk of catching fire, the operator must wear fire-resistant gloves, safety glasses and a visor to carry out the maintenance of the stand and argon exhaust filter.

In no case Thermo Fisher Scientific can be held responsible if the instructions are not respected.

The following material is also necessary:

- A vacuum cleaner with a water circuit for the aspiration and neutralisation of the dust produced by the sparking of the samples.
- Beakers and watch glasses for the cleaning with acid of the stand parts
- Hydrochloric acid at 5% (vol.).
- Demineralised water
- Ethyl alcohol
- Paper tissue

Particular Procedures

Stand and Special Filtering Device Maintenance

The maintenance of the stand components and of the special filtering device is fully described in the *Mg Filter Kit* manual. You must strictly follow the directions written of this manual.

When the instrument is a multi bases one, a dual argon exhaust system with a commutation valve is installed. Concerning the maintenance of the traditional filter used for the other bases than the Mg base, refer to the procedure described in the *Argon Outlet Filter* section of the *Routine Maintenance* chapter of the present manual.

For the cleaning of the stand components (table, hard metal disk, insulator, electrode, cylinder), refer to the *Cleaning of Stand Components* section below.

Cleaning of Stand Components

The cleaning directions given in this manual (sections *Cleaning of the Large Electrode* and *Cleaning of the Stand and the Sparking Chamber* of the *Routine Maintenance* chapter) can be followed. However the use of acid for the cleaning of the analytical hardware is efficient in order to limit contamination sources. But the products to be used are toxic and present a real potential risk of burns by acid.

The maintenance with acid described in this section can be executed only if you have the availability of a chemistry laboratory or at least a working place under a ventilated vault. The use of concentrated acid implies that this maintenance must be done by qualified personal only, under the supervision of a chemist or a metallurgist.

Only trained and qualified personnel must handle the acids.

In no case Thermo Fisher Scientific can be held responsible in the event of accident due to handling of the chemicals products used.

If you do not have the equipment nor the competences, forget this solution.

The acid that must be used for the cleaning of the hardware used with the Mg base is the Hydrochloric acid (HCl) at 5% (vol.).

The analysis table and the bottom of the sparking chamber cannot be cleaned with acid! The cleaning must be done as following:

- Clean the bottom of the sparking chamber with paper tissue if necessary slightly moisten with ethyl alcohol if the part is dirty. Let well dry.
- Clean conscientiously the analytical table with a vacuum cleaner and then with paper tissue slightly moisten with ethyl alcohol, because the table cannot be cleaned with acid.

The electrode and the insulator can be cleaned with acid according to the following directions:

Electrode cleaning

Plunge the electrode tip for 3 cm in HCl acid 5% (vol.) during approximately 1 minute (until the bubbles stop), rinse with demineralised water and wipe with paper tissue.

Insulator cleaning

Usually a simple cleaning with paper tissue is enough. But when the cleaning with paper tissue leaves blackish tracks, plunge the part for some seconds in HCl acid 5% (vol.), rinse with demineralised water and wipe with paper tissue.

Other Subjects

For all the other parts concerning the Mg filter kit, refer to the special *Mg Filter Kit* manual.

For all the other maintenance subjects not explicitly described in the special *Mg Filter Kit* manual or this appendix, refer to the *Routine Maintenance* chapter and its *Summary Table* section.

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