Principles of the high pressure SEM – Applications – Limitations

C. Mathieu

Université d'Artois - Centre de calcul et de Modélisation de Lens – Faculté Jean Perrin – SP 18 -62307 Lens cedex - France

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Abstract. This paper deals with the different kinds of high pressure SEM. The beam-gas interactions and the different electron detectors are described. Examples of applications are given. The limitations for the X-ray microanalysis are discussed. The main effects are shown and practical solutions are proposed in order to limit these effects and the different correction methods described in the literature are presented.

Introduction

Conventional scanning electron microscopy (SEM) is widely used as an analytical tool. However, there are several limitations on the types of samples which may be observed. When a specimen consists of a non-conductive sample, or is not properly grounded to the specimen stub, charging occurs. Charging is the build-up of an excess of electrons on the surface specimen which causes many undesirable artefacts. Both secondary and backscattered electrons used for SEM observations are significantly affected. The negative field from the charging surface deflects the negative incident beam from its intended course. Analysis by WDS or EDS is compromised because of incident beam deflection and image drift, making the analysis less accurate and reproducible. Elimination of specimen charging can be accomplished :

- ***by the deposition of conductive films on the specimen surface*** which is then grounded to the specimen stub. The excess of electron charge can now flow to ground via the conductive films thereby eliminating charge. This way is largely used in the conventional SEM.
- ***by reducing the accelerating voltage below the charging point***. This is the point where the amount of charge being put into the sample by the primary electron beam is equal to the amount drained off, the point of charge equilibrium. This way is largely used with the FEG-SEM.
- ***by the introduction of gas (air gas, water vapour, nitrogen gas) in the specimen chamber***. In this case, the collision of the electron beam with gas molecules produces positives ions near the specimen chamber. These ions can then combine with excess electronic charge on the surface and in this way neutralise the sample surface. This way is used in the high pressure Scanning electron microscope (HPSEM). This term due to Farley and Shah[1-2] has been introduced to distinguish these techniques from conventional high vacuum techniques such as regular SEM and low temperature scanning electron microscopy. This includes a variety of techniques reported in the scientific and commercial literature, e.g., environmental scanning electron microscopy (ESEM)[3-8], WET-SEM, controlled-atmosphere scanning electron microscopy (CAT-SEM), Low Vacuum SEM and Variable pressure scanning electron microscopy (VPSEM)[9-10].

The aims of this paper are to describe the principle of the high pressure SEM, the applications and the limitations for the X-ray microanalysis.

1.The high Pressure SEM
1.1Principles of the high pressure SEM

The high pressure SEM possesses two way of imaging the sample

- High vacuum mode (HV) (10-3 Pa).
- High gas pressure mode (HP)(1- 1300 Pa).

In the first mode, the HPSEM operates exactly like a conventional scanning electron microscope. Topographic images of the specimen are obtained with the secondary electron detector while compositional detail is revealed by the backscattered electron detector. In this mode, the classical limitations exist for the image quality. Charging can be avoided by conductive coating or by reducing the accelerating voltage below the charging point. When the microscope is used at lower accelerating voltage, its resolution is greatly reduced. This implies that the resulting images will not provide information of the quality obtained at a higher accelerating voltage. Furthermore, excitation energies are usually not sufficient for EDS or WDS techniques.
Moreover, with a biological or a hydrated sample, the high vacuum induces an evaporation of water inside the specimen and a dehydration of the sample is obtained and it is not possible to observe the sample at room temperature in the natural state.
To overcome these limitations, the high gas pressure mode can be employed. The elimination of the specimen charging is accomplished by the introduction of gas molecule in the specimen chamber. The collision of the electron beam with gas molecules produces positive ions near the specimen surface. These ions can then combine with excess of electronic charge on the surface and in this way neutralize the sample surface (see fig 1).

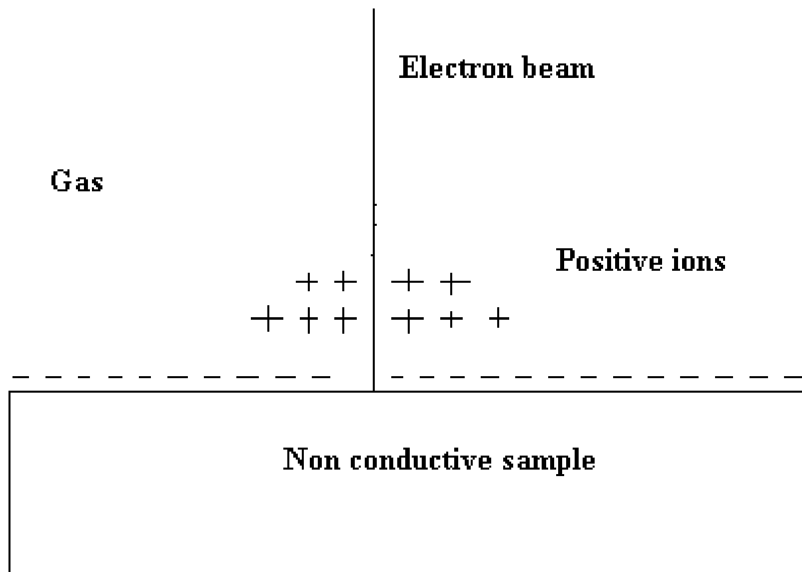

Figure 1 Operating principle of the high pressure mode.

The presence of a gas around the specimen has some important advantages. The main is the suppression of the charge accumulation on insulating specimen. The second is to preserve the natural state for the biological sample and in the case of the electron detection, the gas contributes to the amplification of signals. [5]
Practically, the operator selects the pressure and instructs the computer to raise the vacuum pressure in the chamber until a charge free condition is reached or in the case of a biological sample to raise the pressure in order to limit the dehydration phenomena. The pressure level

can be decreased or decreased through a menu and adjusted via the computer feedback mechanism. The comparator reads the vacuum menu input and the specimen chamber pressure and at the same time adjust the needle value. Accordingly, this dynamics adjustment provide a vacuum level which should remain constant. In these circumstances, the chamber pressure can be considered as a new parameters, available for adjusting imaging quality.
The presence of a low vacuum in the specimen chamber is an important feature of the SEM apparatus. Indeed, the optical column is separated from the specimen chamber by a PLA (pressure limiting aperture). The differential pumping permit to have a pressure up to 1300 Pa in the case of the ESEM and to have a pressure up to 300 Pa in the others HPSEM. The ESEM has been defined as an SEM capable of maintaining a minimum of water vapour pressure of at least 609 Pa in its specimen chamber. This pressure corresponds to the saturation pressure of water at 273 K and constitutes a natural threshold, above which water can be maintained in its liquid phase. At the room temperature, the corresponding temperature is higher and an ESEM can operate also at this or higher pressures. This capability to observe water in its liquid phase is the main difference with the other commercial HPSEM.
The gas in the specimen chamber is generally water vapour in the ESEM and air or nitrogen gas in the others HPSEM. The operators can change the nature of the gas in the SEM chamber and it is possible to put mixture of gas in function of the application.
In the next part, we want to present the interaction between the gas and the electron beam and the consequences for the electron detection.

1.2 The Beam-gas interaction and the electron detection

1.2.1 The ionisation process.

The electron beam propagates unhindered until it approaches the final aperture and, form a particular point onwards, it undergoes significant scattering. The pressure is generally uniform throughout the specimen chamber, except for a small region in the neighbourhood of the aperture. The presence of gas results only in scattering and removing fraction of electrons from the original beam into a broad electron skirt that surrounds the original skirt. A schematic representation of possible ionisation events is given in figure 2 .

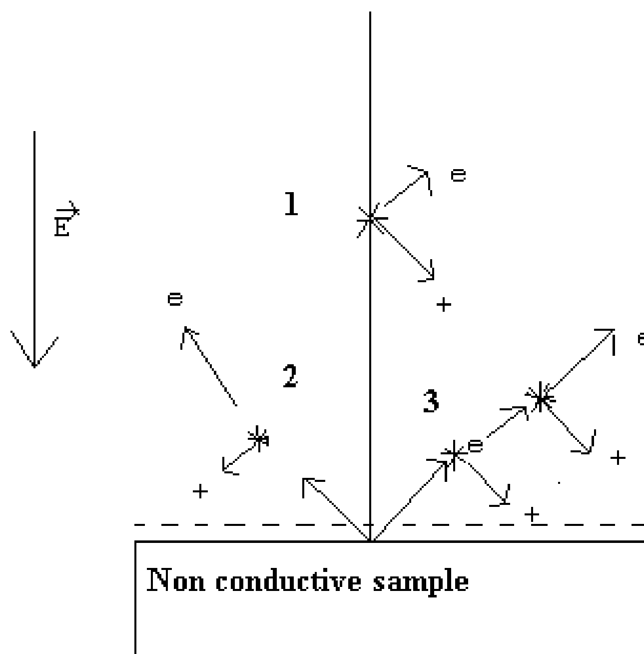

Figure 2 Schematic diagram of ionising collisions in a low pressure gas above a charged non-conducting specimen.

Gas ionisation results from collisions initiated by (1) incident electron beam electrons, (2) backscattered electrons and (3) secondary electrons emitted from the specimen. Further ionisation events follow since each ionising collision liberates a low-energy electron that can be accelerated by field E until its energy exceeds the ionisation energy of gas molecules. [11]. There is a significant probability with each collision that an additional electron (called environmental secondary electron)will be liberated so that an avalanche process ensues. This phenomena is used in the environmental secondary detector in the ESEM.

Finally, inside the specimen chamber, we can distinguish the following electrons

Backscattered electrons.

Environmental secondary electrons.

The secondary electron emitted from the specimen has not sufficient energy to reach the Everhart- Thornley detector and the following mode of detection have been employed.

1.2.2 the electron detectors

The Backscattered mode

Backscattered electron imaging with high gas pressure in the specimen chamber has shown itself to be a useful technique in the scanning electron microscope. The backscattered electron have a sufficient energy to excite the detector. For example, specimen may be surrounding by air or nitrogen gas to inspect non conductive surface [11-13] or by water vapour in biological applications [14-15]

Practically, the signal to noise ratio decreases and the image quality decreases at high pressure. The emission of the backscattered electrons at the impact point is reduced due to the skirting effect. Moreover, the interaction between the gas and the primary electron beam and also the interaction of the emitted backscattered electron with the gas add a constant level of noise to the useful signals form the specimen. (see Fig 3 A)

-Emissive mode

The emissive mode of detection has been employed using a ‘gaseous detector device’ (GDD see Danilatos [8] for a review). This is a collecting electrode which under working conditions, is placed in the vicinity of the specimen and it is positively biased. The electrode collects emitted electrons, along with the electrons generated by them and the primary electrons due to ionisation processes.

Practically, in order to increase the signal to noise ratio, the operator can increase the gas pressure and can modify the potential on the collecting electrode to improve the avalanche process.

- Specimen current mode and biased current mode

Farley and Shah [1-2,16] reported images of a quality comparable to that obtained by the Everhart-Thornley detector could be obtained by a new detection mode. They called this new mode of detection the bias specimen current detection mode. A biasing electrode is used above the specimen to influence the trajectories of the charge carriers and hence image contrast. The specimen is connected, via the specimen stub, to the virtual earth terminal of a charge sensitive amplifier to collect the current generated in and around the specimen. It has been successfully shown that the current can be collected from the specimen for the purpose of image generation, for both conducting and non-conducting specimen. This mode is now used in the other HPSEM. [17]

Practically, in order to increase the signal to noise ratio, the operator can increase the gas pressure and can modify the potential on the collecting electrode to improve the avalanche process.

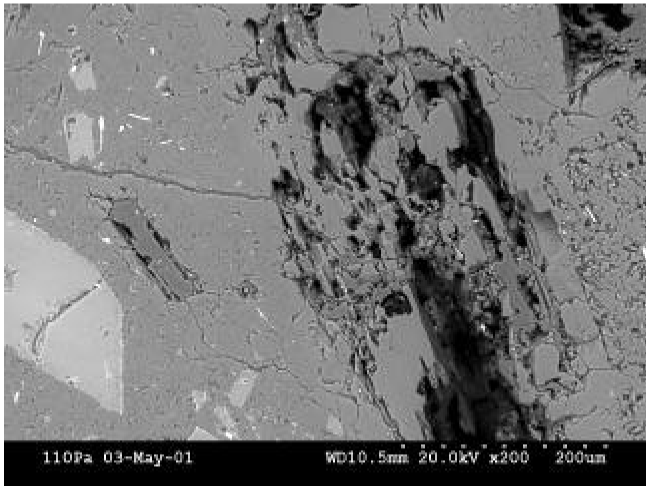

Figure 3 a Image of a geological sample with the backscattered detector (U = 15 kV, P = 100 Pa with air gas)

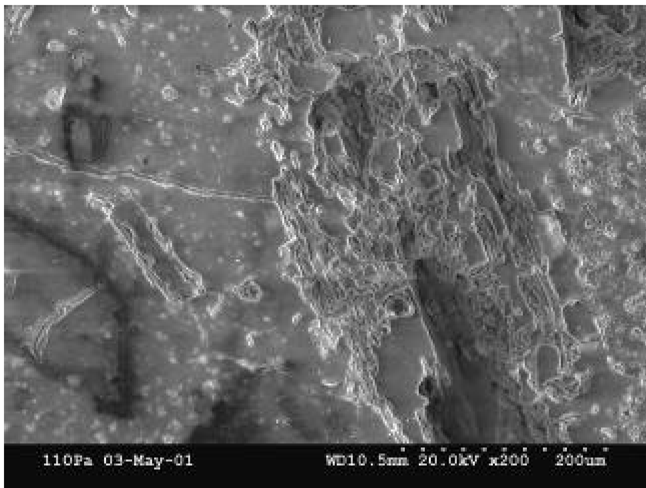

Figure 3 b a Image of a geological sample with the specimen current detector (U = 15 kV, P = 100 Pa with air gas)

2- Applications

The types of applications that the HPSEM is able to tackle are virtually unlimited. Unlike the conventional SEM, which is restricted to clean, dry specimen, the HP-SEM can be used to observe a wide of wet, oily and non conductive specimens.
The main interest is the possibility to observe directly the sample without preparation (no coating).
The following are examples of specimen can be observed with the HPSEM in the high gas pressure mode:
- Insulating materials such as ceramics, plastics, polymers, synthetic fibres, powders, paper products, textiles.
- Plants, food, soil, insect, tissues, petroleum product.
- Hydrated cement, geological sample
-Forensic and archaeological items that prohibit sample preparation and all uncoated sample requiring EDS or WDS analysis.

3-Limitations

The limitations of the HPSEM concerns essentially the interpretation of the contrast in the HPSEM Images and the use of XRMA in the mode of high gas pressure mode.

3-1 limitation for imaging:
The image formation in the HPSEM is due to backscattered electron detector or by Pseudo-secondary electron detector. The interpretation of the images is based of the classical interpretation with a secondary or a backscattered detector in a topographic mode. However, the neutralisation of the surface due to the presence of the gas is more complex and recombination between electron and ions can be took place and several authors have observed an contrast inversion in function of the pressure, the working distance and the potential of the electrode[18]

3-2 Limitation of the use of XRMA in the high gas pressure mode.
The HPSEM can be considered as an universal microscope for all types of sample and as a classical SEM, an EDS or WDS system can be coupled to the microscope. Unfortunately,
the presence of a gaseous environment in the specimen chamber presents serious limitations for the use of XRMA due to three major effects - **loss of spatial resolution** due to beam broadening (beam skirting), **X-ray contribution from the gas atmosphere** due to the interactions between the primary electron beam, the backscattered electrons and the gas, **reduced X-ray count** (interaction between photons and the gas).[19]

3-2-1 Loss of spatial resolution due to beam skirting
Sigee and Gilpin [20-21] proposed a simple experiment to demonstrate the beam skirting. An electron beam is directed onto a layer of carbon with a copper target placed at varying distances from the primary probe area. The skirting effect of the beam within an air atmosphere is shown by the ability to pick up a Cu signal of varying intensity from the central probe area. (see fig4).

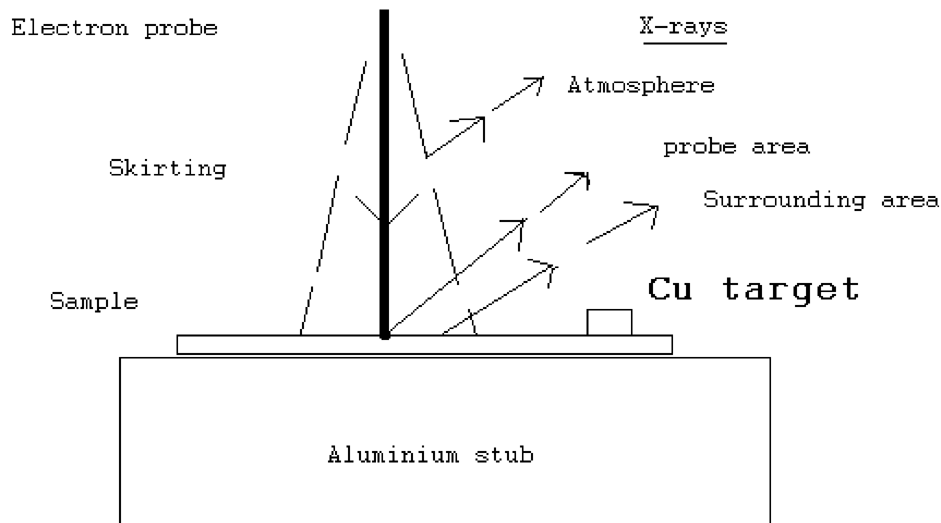

Figure 4 The different effects for the X-ray microanalysis due to the beam gas interactions

Most data were obtained at distances of 100-1000µm from the Cu target. At high vacuum, no Cu peak was detected at these distances. The analytical distance was equal to 25 mm.

At a distance equal to 1 mm, the copper content varied from 2 to 9 % when the pressure ranged from 1 to 270 Pa.(Fig 5) at 15 kV.[22]

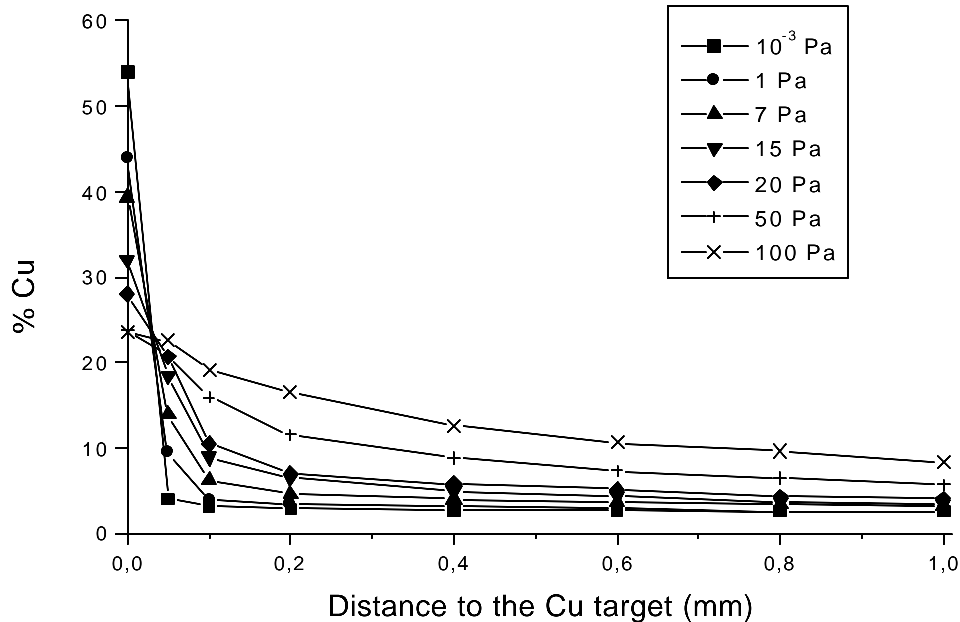

Figure 5 Variation of the Cu content versus the pressure and with the distance to the Cu target

The Cu peaks were always detected over the 100-1000µm range between 1 to 270, indicating a clear skirting effect in the presence of an atmosphere. Beam skirting clearly limits the spatial resolution of X-ray microanalysis.
The skirt effect can be directly related to the average number of collision defined by Danilatos [23]

$$m= p. \sigma. L / k .T$$

where p = pressure, σ = the total scattering cross section of the gas, L = distance from the last pressure limiting aperture to the sample, k = the Boltzmann constant, and T = absolute temperature.
In order to reduce m, the pressure, the working distance and the value of the total ionisation cross section must be reduced. For the total ionisation cross section, a reduction implies an increase of the accelerating voltage. Moreover, the nature of the gas can be changed in order to choose gas with a low atomic number like helium [19, 24-25].
The spatial resolution can be improved with the use of high accelerating voltage and low working distance, low pressure and a gas with a low atomic number.

3-2-2 X-ray contribution from the chamber atmosphere
Passage of the electron beam through the specimen chamber atmosphere leads to the generation of characteristic and continuum X-rays from the gas molecules.
In order to illustrate this effect , a sample which contains Na, Al, Si and O is analysed at three different accelerating voltage (5, 10 and 15 kV).The sample is deposed on a aluminium stub.
With the same excitation conditions, the effect of introduction and increased levels of air atmosphere was investigated by collection of X-ray from the sample. X-ray emission spectra at high vacuum indicated only peaks of O, Na, Al and Si.
Figure 6 shows the variations of the ratio of the oxygen content at different pressure on the oxygen content at 1 Pa which is used as a reference at three different accelerating voltage. The

curve obtained at 5 kV show an important increase of this ratio. This behaviour is not observed at 15 kV.

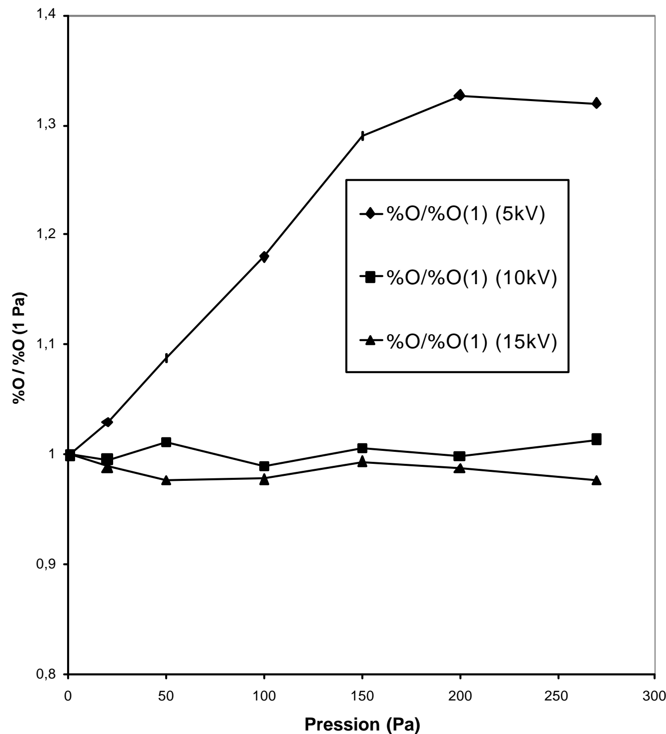

Figure 6 Variation of the %O/ % O (1 Pa) ratio with the accelerating voltage

The air atmosphere into the specimen chamber implies only the generation of an oxygen signal, which increased with atmospheric pressure. The presence of an atmospheric X-ray contribution clearly presents problems for the determination of oxygen content in the analysed specimen.

X-ray contribution from the atmosphere clearly limits quantitative X-ray microanalysis. Various operational parameters can be optimised to reduce this effect including atmospheric pressure and nature of atmospheric gas.

Atmospheric pressure. Chamber pressure should be kept as low as possible

Nature of atmospheric gas In order to reduce the X-ray contribution from the atmosphere, a practical solution is to choose a gas such as H_2 or He. Indeed, the atmospheric contribution will not detect by XRMA.

3-2-3 Reduced X-ray count

Introduction of an atmosphere into the specimen chamber can lead to a marked fall in the total counts of the X-ray spectrum. In the HPSEM, with the same excitation conditions, air atmosphere has an important effect with the reduction of the total X-ray counts. This effect is more important at low accelerating voltage. The decrease of the total counts can be explained by reduced electron beam penetration to the specimen due to electron scatter and also probably by the absorption of X-ray photons in the gas at high pressure

In order to reduce this effect, the choice of gas with a low atomic mass such as hydrogen gas, helium gas can be an interesting solution.

3-2-4 The correction methods

Two basically different correction methods have been described by Bilde Sorensen and Appel [26-27] referred to as the beam stop and pressure variation procedures.

Beam stop method.

One version of this procedure involves the use of a needle (composed of a known element not detected in the sample) that can be inserted over the specimen to act as a beam stop for the central (unscattered) electrons but not the peripheral beam skirt. The spectrum obtained with the beam stop in position contains x-rays derived from the known element (beam stop) plus the area covered by the beam skirt. The pure spectrum from the central probe area can be obtained by removing the characteristic peaks of the known element from the first spectrum and substracting the remaining spectrum from the second.

Pressure variation method

This approach is based on the fact that intensity of skirt varies with chamber pressure, and thus correction for electron scattering can be made by obtaining x-ray spectra at different chamber pressures. According to Danilatos[23] at any particular pressure the fraction of unscattered electrons is given by the equation:

$$I/Io = \exp(- p\sigma L/kT)$$

where p = pressure, σ = the scattering cross section of the gas, L = distance from the last pressure limiting aperture to the sample, k = the Boltzmann constant, and T = absolute temperature.

The above expression can be used to relate the measured count rate (C_T) from a particular element in the sample to counts rates at zero scattering (C_u) and complete scattering(C_s).

$$C_u = C_u \exp(-pm) + C_s (1-\exp(-pm)) \text{ where } m = \sigma L/kT$$

The factor C_s is unknown, but will be a constant provided that pm is sufficiently low for multiple scattering of electrons to be ignored. Under these conditions, C_u can be derived from two measurements of C_T at different pressures, where p and m are known.

It exists another correction method proposed by Doehne [28] the method is as follows: an X-ray spectrum (A) is acquired under condition of high chamber pressure (2P). Another spectrum (B) is made under identical conditions but at a lower chamber pressure (P). The difference between the two spectra provides information on how decreasing the contribution of the X-ray generated by the skirt electrons affects the overall spectrum. If C is the spectrum at low pressure ($<10^{-3}$ Pa, no skirt effect), then C can be approximating by the following: C = B - ((A-B)*D).

This methods assumes that changes in the lateral extent of the X-ray skirt with pressure are less important than changes in the skirt intensity.D is an empirical factor derived from observation when x-ray background shape of spectrum B is significantly altered by the subtraction of the spectral differences between A and B. The background shape acts as a built in against overcorrection. It exist another correction methods based only on the skirt effect [29]

It is important to notice that these correction methods which have been described account only the skirting effect.

4-Conclusion

The High pressure SEM can be considered as an universal SEM for all types of samples for the imaging. The different detectors have been presented.. However, serious limitations exists with the use of XRMA in the condition of high gas pressure mode. The three main effects have been described. In order to reduce these effects, a good practical solution is to use a gas with a lower atomic mass number like Helium which permits to eliminate the

atmospheric contribution. However, in order to permit quantitative X-ray microanalysis, the correction of all disturbing effects remains a challenge.

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