

8-7-1993

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Marshall, Donald J. (1993) "The Present Status of Cathodoluminescence Attachments for Optical Microscopes," *Scanning Microscopy*: Vol. 7 : No. 3 , Article 10.

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THE PRESENT STATUS OF CATHODOLUMINESCENCE ATTACHMENTS FOR OPTICAL MICROSCOPES

Donald J. Marshall

Consultant

Post Office Box 12, Bedford, MA 01730, U.S.A.

Telephone number: 617-275-4695

(Received for publication February 28, 1993, and in revised form August 7, 1993)

Abstract

The serious use of cathodoluminescence (CL) in petrography began about 30 years ago with the electron microprobe analyzer. Investigators soon began to use simpler instruments mounted directly on optical microscopes - cathodoluminescence microscope attachments (CMAs).

A major advantage of the CMA, compared to a scanning electron microscope (SEM) or electron microprobe analyzer (EMPA), is the capability to switch quickly between CL observations and high quality conventional optical microscope observations. Beam currents available in the CMA are higher than in the SEM or EMPA and one sees an instantaneous real time true color display of the CL pattern.

CMAs are based on either cold cathode or hot cathode electron guns. Typical operation is at 0-30 keV, 0-1 mA, and a focused beam. Modern cold cathode systems include regulation of current and voltage in the discharge. Conductive coatings on samples are not required with cold cathode guns.

Recent developments include accessories for energy dispersive spectroscopy (EDS), cooled stage operation, and improvements in systems for spectral analysis of CL emission.

CMAs are finding wide application in the earth sciences and also in the study of ceramics, glasses, synthetic crystals, archaeological specimens, and other areas.

Key Words: Cathodoluminescence, cathodoluminescence microscope attachments (CMA), cooled stage, cold cathode electron gun, hot cathode electron gun, CL spectroscopy.

Introduction

When an energetic electron beam impinges on certain types of insulating or semiconducting materials, visible radiation is produced. This process is called cathodoluminescence (CL). The application of cathodoluminescence in the earth sciences received a strong boost in the early 1960s when Smith and Stenstrom (1965) and Long and Agrell (1965) published CL results from their electron microprobe analyzer (EMPA) work. These studies showed the tremendous potential for the use of electron-induced luminescence of minerals to distinguish zonation in cements, to distinguish different generations of quartz and feldspar, and to provide, sometimes, spectacular displays of minor amounts of zircon, apatite, and other minerals. Immediately after these publications, the development of optical microscope attachments for CL studies, cathodoluminescence microscope attachments (CMAs), took place.

Work done with the CMAs has confirmed and expanded upon the EMPA results and there are now abundant examples in the geological literature which illustrate the additional information that CL reveals. Elaborate zonation is often seen in carbonate cements that appear uniform in plane light observations. Quartz cement is often easily distinguished from detrital grains. Even zonation within the quartz cement can sometimes be observed. Single crystals of apatite, fluorite, calcite, and other minerals that appear uniform in plane light, sometimes reveal complex zonation patterns (Mariano, 1988). The applications to alkaline rocks, to fentization studies, and to minerals containing rare earth elements have been extremely fruitful (Mariano, 1988).

Because of the promise shown by many of the samples studied with the EMPA, it was almost immediately recognized that a simple device which mounted directly on a good petrographic microscope would be useful. A number of investigators designed and built one of these simpler systems (Long and Agrell, 1965; Sippel, 1965). Sommer (1972) described a system which simply used a Tesla coil and a glass vacuum bottle. Commercial units soon became available (Herzog *et al.*, 1970). Now there are several hundred laboratories throughout the world that are using CMAs. Most of these are based

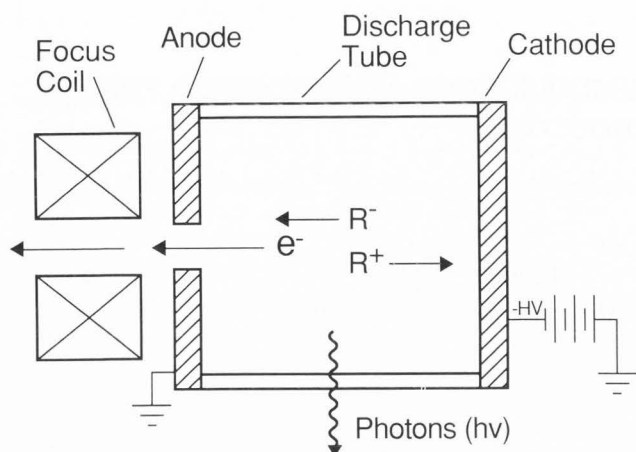


Figure 1. The cold cathode discharge contains electrons (e^-), which are predominantly accelerated towards the anode, and positive ions (R^+) which are predominantly accelerated towards the cathode. In addition, there are metastables (R^*), negative ions (R^-), and photon emission including X-ray photons ($h\nu$).

on cold cathode electron sources although a few use hot cathodes. Both sources provide maximum beam energies in the 15 to 30 keV range. There has been a parallel development in CL studies and instrumentation with the scanning electron microscope (SEM) and EMPA and many of these are fitted with some form of CL detector. We will not review the CL systems for use on SEMs or EMPAs in this paper though significant developments are taking place in this area also (Remond *et al.*, 1992; Wright, 1991; Wright and Kearsley, 1991).

An advantage of the CMAs, compared to the SEM and EMPA, is that they are relatively inexpensive. They also provide the means to do CL work interchangeably with conventional plane polarized light observations on a good quality petrographic microscope on standard thin sections. For those CMAs which use a cold cathode electron source, conductive coatings and other special sample preparation procedures are not needed.

The purpose of this paper is to describe several of the CMAs and to compare the advantages and disadvantages of different electron beam-sample-light source geometries.

Instruments Based on Cold Cathode Electron Gun

The cold cathode source is a steady discharge between a cathode at a negative high voltage and an anode at ground potential. For high voltages in the 6 to 30 kV range, this discharge can be established if the pressure in the region between the electrodes is in the 10 to 100 millitorr range.

The cold cathode discharge is a complex environment which contains not only the desired electrons but also positive and negative ions, metastables, free radicals, etc. (Figure 1). The discharge appears as a visible

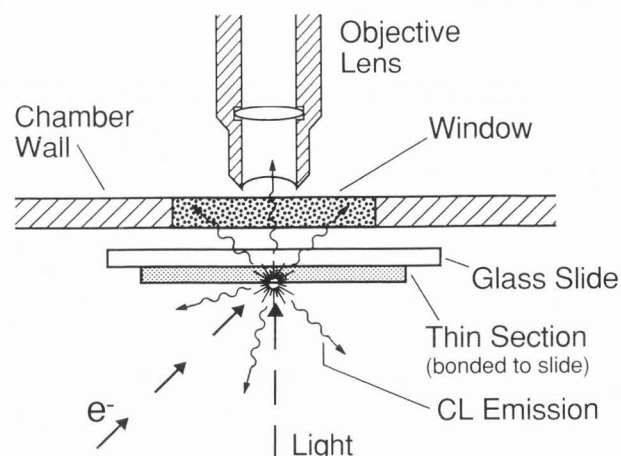


Figure 2. Electron beam-sample geometry used in the design of Sippel (1965). The window indicated in this illustration and in later ones should be leaded-glass for X-ray safety. The light beam indicated is the normal light source on the microscope. This light source is normally turned off when the CL is turned on and vice versa. Thin section is not shown to scale.

plasma to the observer.

Energetic electrons in the discharge pass through an anode aperture into the sample region. For the usual range of beam energies used, the discharge is visible right up to the point of contact with the sample since there is a continuous plasma environment along the beam path.

Cold cathodes are popular because they are rugged and inexpensive, and require only simple vacuum systems. More importantly, there is no need for conductive coating of the sample because the plasma environment in the discharge provides charge neutralization. The details of the neutralization process are complex, and are difficult to analyze theoretically, but the process is very effective. It is the same process that takes place in those SEMs which operate with the specimen chamber at elevated sample pressures (Danilatos, 1990).

Most users operate cold cathodes with room air leaked in, although a few use helium as the support gas. The helium discharge is a little easier to control than the air discharge. Usual vacuum systems consist of a vacuum chamber with sample manipulators, a mechanical vacuum pump, and a leak valve. The electron gun region is at essentially the same pressure as the main sample chamber. Differential pumping is not used.

Review of instrument designs based on cold cathode electron sources

The details of the vacuum chamber arrangements will not be shown but the essentials of the electron beam-sample-light beam intersection geometry used in several designs are useful to review.

Sippel (1965) published one of the first cold cathode designs. The initial unit could be operated at voltages up to 25 kV AC and later he converted it to DC and

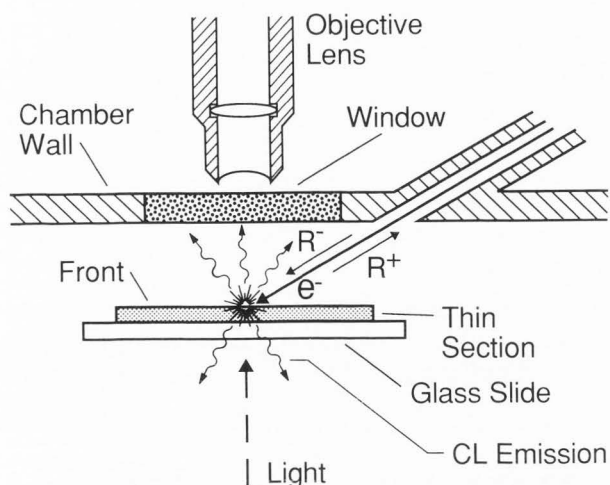


Figure 3. Electron beam-sample geometry used with electron beam and light source incident from opposite sides. Early instruments with a rotating vacuum chamber stage could be used in this configuration or in the configuration shown in Figure 2. Positive ions (R^+) and negative ions (R^-) are present in the discharge. The positive ions tend to be accelerated away from the sample. Negative ions are present in only small amounts when either air or helium is used as the support gas.

a focused beam. The basic geometry used by Sippel is shown in Figure 2. The sample is an uncoated thin section which is viewed from the back (i.e., through the glass slide, see Figure 2). This geometry makes it convenient to mount the CMA directly on many different styles of microscopes. Transmitted light (TrL) studies can be made in the normal fashion. This geometry is only suitable for thin sections and not for slabs or loose grains because the CL must be viewed through the sample.

Adequate working distance of optical microscope objective lenses is always a matter of concern with the CMAs and the smaller the value of this parameter the greater the choice of objectives. This distance is minimized with the general arrangement shown in Figure 2. The minimum working distance is slightly greater than the sum of the thickness of the glass slide [typically 1-1.25 mm (0.040-0.050 inches)], the thickness of the thin section itself (30 μm), and the thickness of the vacuum window. The latter is usually 3 mm thick leaded-glass so the minimum working distance could be as short as 5 mm for this design.

For most geological thin sections, viewing from the back of a coated thin section is acceptable. However, some authors (e.g., Davies, 1974) have pointed out that absorption effects can be an important problem in thicker samples and that results, especially CL emission spectra, may differ from those obtained when viewing is done from the same side as the electron beam incidence. The absorption effect does not seem to be important for normal thin section studies.

The details of several other early CMA designs that have appeared in the literature [Le Poole *et al.*, 1968 (hot cathode); Harmer *et al.*, 1968 (cold cathode)] are summarized by Marshall (1988).

Commercial designs based on cold cathode electron sources

The first commercial instruments (Nuclide Corporation) were similar to Sippel's design (Figure 3). Beam energies were variable up to 15-18 keV and the beam was focusable. They provided for mounting the CMA on a conventional petrographic microscope with the objective viewing from above. The electron beam is either incident from the top or, by rotating the CMA stage by 180 degrees, the electron beam could be incident from the bottom. This gave the user the choice of viewing from the front of the thin section, with the longer working distance requirement, or from the back of the thin section with the shorter working distance requirement.

This basic geometry, with viewing from the front of the thin section, is used in the present day Technosyn (now Cambridge Image Technology Ltd., P.O. Box 21, Cambridge, CB1 4UN, U.K.) commercial CMA (Barker and Wood, 1987). This instrument has a fixed beam which strikes the thin section at an angle and the samples are viewed from the front side where the beam strikes (Figure 4). The sample holder/mounting accepts samples up to 6 x 7.5 cm in area and can be adjusted to allow the study of thin sections or thicker samples (slabs) up to 17 mm thick. The maximum beam voltage is 30 kV and the maximum beam current, at 25 kV, is 0.4 mA. A focusing accessory is optional.

In the commercial instrument developed by Nuclide Corporation and now produced by PATCO (Premier American Technologies Corp., 1155 Zion Road, Bellefonte, PA 16823), the Luminoscope[®] (Nuclide Corporation, State College, PA), the geometry is arranged so that the beam is incident from above the sample but the point of the beam impact is variable in the horizontal plane, facilitating lining it up with the optical axis (Herzog *et al.*, 1970). Viewing is done from the front of the sample. The beam is initially horizontal and then is deflected onto the specimen (Figure 5). By moving the deflecting magnets laterally, the intersection point of the beam can be brought to the optical axis for a range of sample thicknesses. This arrangement provides considerable flexibility in the choice of samples. They can be thin sections, slabs, chips, or even loose grains. Some operators feel that the Technosyn arrangement, with a fixed beam position and no deflection magnets, is easier to use because the operator is freed from one more adjustment. However, it may be less flexible in use for irregularly shaped samples.

The beam voltage on the present Luminoscope is continuously variable from 0 to 30 kV, the beam current is continuously variable between 0 and 2 mA, and the beam at the sample can be focused to 1 mm diameter or defocused to diameters as great as 2 cm for macrophotography or other purposes. Both the beam current and beam voltage are regulated (Marshall *et al.*, 1990).

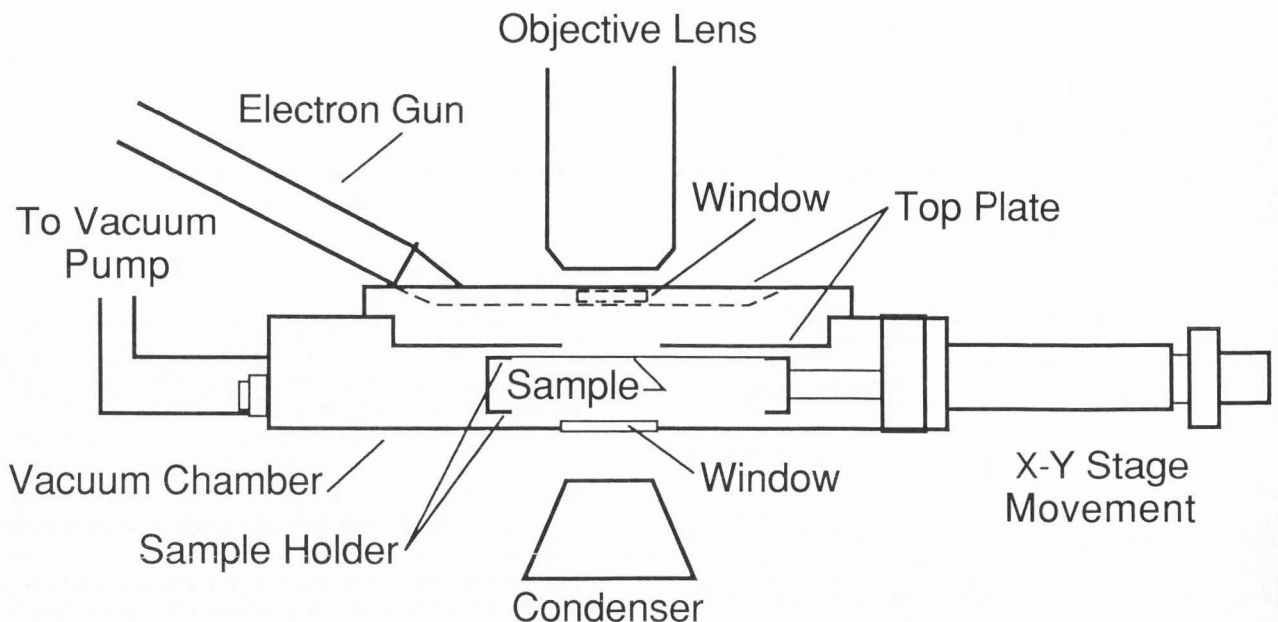


Figure 4. The geometry used in the Technosyn instrument. The sample CL is viewed from the same side that the beam is incident on. The optical axis/electron beam intersection geometry is fixed. (From Barker and Wood 1987).

The overall size of the vacuum chamber shown, not including the electron gun and focus coil, is about 10 cm x 18 cm with a thickness of about 3 cm. The entire area of a thin section as large as 5 cm x 7.5 cm can be studied. Sample thickness can be as large as 6 x 8 mm.

The minimum working distance requirement for both of the commercial designs (Technosyn and Luminoscope), where the CL emission is observed from the top of the sample, is typically 8-10 mm. This minimum distance is established because there must be adequate room for the leaded glass window and for the beam to pass between the window and the sample. A number of standard commercial microscope objectives with adequate working distance (> 10 mm) are now available for objective magnifications up to 40X, though most work is done at 20X or lower (see, Table 3.3 in Marshall, 1988).

The transmission of the objective lens is proportional to the square of the ratio of the numerical aperture (NA) to the magnification (M) (Eastman Kodak Co., 1980). At higher magnifications, it is important that the objective lens have the highest possible numerical aperture to maintain good transmission.

The vacuum surface of the viewing window is quite close to the electron beam and the specimen surface in these designs and it will become coated and require frequent cleaning. The coating reduces the absolute transmission and also changes the transmission function of the window, i.e., the variation of transmission with wave length.

When the CMA is mounted on the microscope stage, with vacuum lines and electrical cables attached, it is not feasible to rotate the sample in the normal fashion for polarized light observations. Some older microscopes have top and bottom polarizers which are coupled together and can be rotated about a fixed sample. These are useful with a CMA. Special polarizer assemblies have been designed to straddle the CMA vacuum chamber but their use increases the objective lens working distance requirement.

Instruments Based on Hot Cathode Electron Guns

One of the first optical microscope CL instruments described was that of Long and Agrell (1965). It was mounted on a standard optical microscope and used a hot cathode with misaligned beam apertures to eliminate filament light. Energies up to 9 keV were provided. The instrument described by Le Poole *et al.* (1968) used a hot cathode, provided for beam energies up to 30 keV, and included focusing and deflection of the electron beam. Iijima *et al.* (1983) described a 20 keV system, equipped with a spectrometer.

The interest in hot cathode CMAs has continued, although they are not yet a standard commercial item. To some extent the interest in hot cathode instruments was generated by interest in looking at quartz CL which is often quite weak. The CL intensity of most minerals, including quartz, increases strongly with beam energy and energies up to 30 keV were used by Zinkernagel (1978) who published his hot cathode design along with many beautiful and important examples of quartz CL.

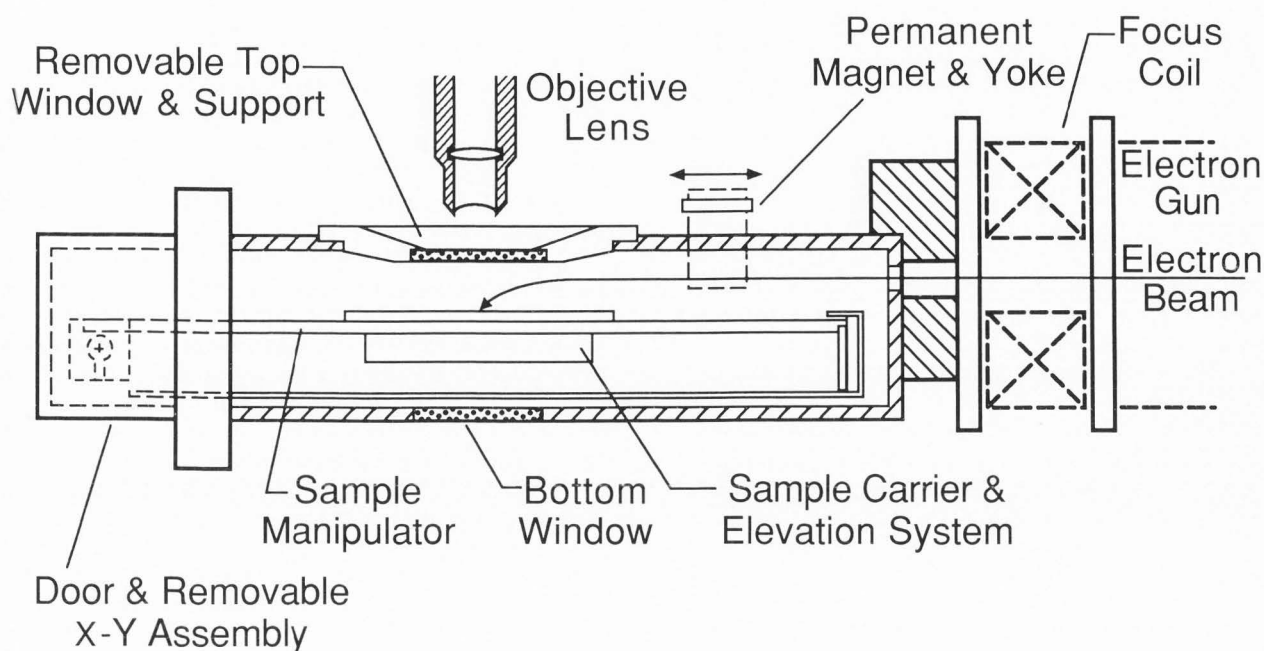


Figure 5 (above). The geometry used in the Lumino-scope. The sample CL is viewed from the same side that the beam is incident on. The beam can be positioned by the deflecting magnet assembly to adapt to different sample thicknesses or to observation of grains or chips.

In Zinkernagel's instrument, the electron beam is incident at an angle on the coated specimen and the CL is viewed from the back.

Subsequently Ramseyer *et al.* (1989) published another hot cathode design which is similar conceptually to that of Zinkernagel. The electron beam is normally incident as shown in Figure 6. They use a hot filament, which is off axis, to reduce the amount of direct filament light reaching the specimen. The TrL beam is introduced via an optical system which is moved in and out of the electron beam path as needed. A special feature of this system is a polarizer assembly which enables the polarizer and analyzer to be turned simultaneously in the crossed position.

The sensitivity of this instrument is excellent and there have been extensive publications on its use, particularly for quartz samples (Matter and Ramseyer, 1985; Ramseyer *et al.*, 1988; Ramseyer and Mullis, 1990) and faintly luminescing carbonates (Barbin *et al.*, 1991).

Walker and Burley (1991) described a hot cathode instrument which evolved from their early work dating back to 1972. This instrument provides electron energies up to 25 keV and the beam can be focused, deflected, and pulsed. The latter provision is useful in that it permits one to measure luminescence decay times and to use lock-in amplifier techniques to measure spectrally analyzed signals of low intensity. They have the capability to do spectral analysis and also have provision for cooling the samples to temperatures approaching 6°K.

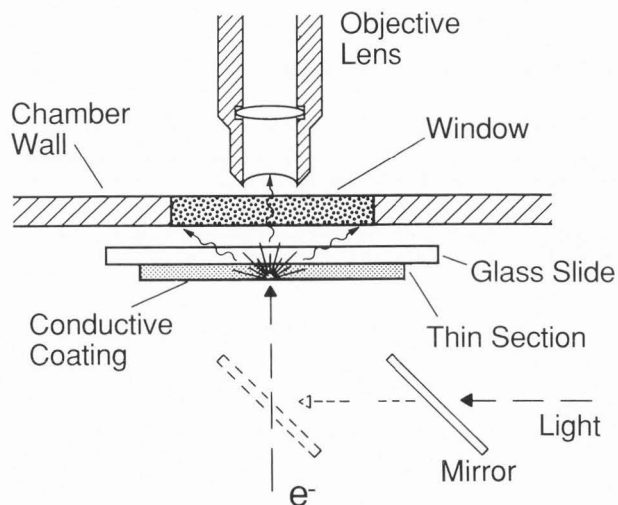


Figure 6. The type of electron beam-sample geometry used by Zinkernagel (1978) and Ramseyer *et al.* (1989). The electron beam is formed from filaments off axis to minimize direct filament light from reaching the sample. The mirror is moved into position when TrL observations are made and moved out of the path when the electron beam is on.

In general, the required working distances for these hot cathode designs are short and may be 4 mm or less. If all other parameters are equal, a shorter working distance requirement means that a lens with a higher NA can be used. Also coating of the inside surface of the viewing window is less important in the hot cathode designs because the beam and sample surface are not immediately adjacent to the window. Both of these features are important in improving sensitivity.

In all of the hot cathode instruments described, a conductive coating is required on the sample surface to prevent electrical charging and viewing is done from the back. Aluminum, gold, or carbon coatings are commonly used. The coating is very thin so the electron beam and the plane light source beam can pass through it. In addition to preventing charging, the conductive coating gives enhanced intensity because the CL is initially emitted over a sphere and the emission, which is initially directed away from the microscope objective, is partially reflected by the coating which functions also as a mirror.

These hot cathode instruments have produced excellent results but they are considerably more expensive than the cold cathode CMAs and in use by only a small number of laboratories. The present designs require viewing from the back of a coated thin section. Slabs, chips, opaque specimens, and loose grains cannot be (easily) studied. Also the existing designs are not readily portable from one microscope to another and may require the use of a fully dedicated microscope system. The cold cathode instruments, in contrast, are easily mounted and demounted and the microscope can be used for other purposes.

The sample change/pump down times are about 30 to 60 seconds for the cold cathode systems and may be about 10 minutes for the hot cathode systems which require a lower chamber pressure. The cold cathode CMAs require only a mechanical vacuum pump whereas the hot cathode systems require a more elaborate vacuum system with some form of high vacuum pump as well (diffusion pump, ion pump, or turbo-molecular pump).

Hot Electrons and Cold Electrons

There has been a considerable amount of informal discussion about the variations in results between the cold cathode and hot cathode instruments. This discussion has touched on both intensity and the revelation of certain features.

The effective CL intensity obtained with the hot cathode instruments (i.e., that seen by the operator or the camera system) is thought by some investigators to be greater than the intensity obtained with the cold cathode instruments. However, this is difficult to measure because the observed CL intensity depends not only on the exciting beam intensity, and the intrinsic CL intensity of the specimen, but also on the microscope transmission. Unfortunately, many CMAs are mounted on relatively low transmission microscopes and these may introduce as much as a factor of 10 reduction in observed CL intensities, compared to that seen on a high transmission microscope system. The author is unaware of any published studies in which the same sample has been studied with both a cold cathode and hot cathode system on the same microscope. A carefully carried out study of this sort could provide a definitive answer to

the question of whether the hot and cold cathode instruments produce significantly different CL intensities. Such a program is presently in progress by the Society for Luminescent Microscopy and Spectroscopy (SLMS, 1992) and provisional standards will be circulated soon among a large number of laboratories doing CL work. Results will be compared in several respects, including both the revelation of features and CL intensities.

If all other things are equal, an objective lens of higher numerical aperture can be used on a hot cathode instrument like that of Ramseyer *et al.* (1988) and Walker and Burley (1991), because of the short working distance requirements of these instruments. But such an objective could also be used on a cold cathode-based system with the geometry shown in Figure 2, although such an instrument is not presently available commercially.

The "hot cathode versus cold cathode" discussion also generates the question of whether the incident beams are different and whether different instruments may reveal different features. The incident beam in the hot cathode instrument is an essentially pure electron beam with a very small number of negative ions present. In the cold cathode instruments, the beam will also contain ions. For this discussion, we must distinguish between positive and negative ions. (Positive ions are formed by electron bombardment when an energetic electron "knocks off" an outer shell electron from a gas atom or molecule, leaving a positive ion behind. Negative ions are formed when low energy electrons in the plasma environment attach themselves to neutral molecules such as oxygen which have a high electron affinity. The plasma environment is rich in electrons with a wide range of energies so both of these processes can take place.) We must also distinguish between ions of low and high energy. In the earliest cold cathode instruments, which used AC power supplies and an undeflected beam (Figure 3), energetic positive ions and negative ions in the discharge would bombard the sample on alternate cycles and this ion bombardment damages some samples very quickly, reducing the CL intensity. With the DC power supplies used for all modern instruments, only negative ion bombardment can occur and negative ions are much less abundant than positive ions so the damage is less. This ion bombardment damage would be expected to be greatest in those geometries where the beam is undeflected (Figure 3).

In the geometry which uses a deflected beam, the magnetic field strength is only sufficient to deflect the electrons and this means that the much heavier negative ions experience almost no deflection and will not reach the sample (Figure 7). It is correct that ions are formed along the entire electron beam path, right up to where the beam strikes the sample. But those ions formed inside the chamber, after deflection of the electron beam, are in an essentially zero electric field and so they cannot be accelerated to a significant energy. They are more nearly thermal energy ions (25 meV to a few electron volts of energy) and are not expected to be important in producing luminescence or in causing damage.

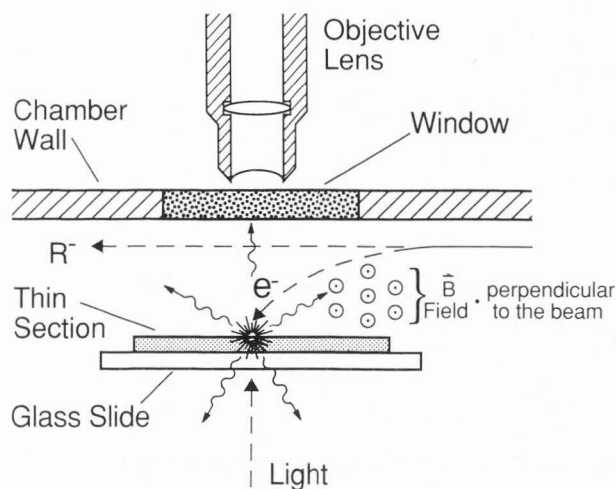


Figure 7. Cross-section of the beam path in a cold cathode system with a deflected beam. Electrons are sharply deflected but ions present in the beam are only very slightly affected by the deflecting magnet field because of their much higher mass.

A careful study, comparing results from the same sample(s) on hot and cold cathode systems, and cold cathode systems with and without deflected beams, would be a valuable contribution. The standards program of the SLMS, referred to previously, may provide this data.

Beam Energy, Beam Current, Beam Power and Beam Power Density

These parameters define the important characteristics of the electron beam. They are sometimes confused and several errors have made their way into the literature so it may be worthwhile to define them.

The beam voltage is the voltage provided by the power supply and usually ranges between 0 and 30 kV. It is the potential difference between the cathode, where the electrons originate, and the anode, where they have attained their final acceleration. The energy of a single electron is the product of the charge of the electron and the voltage difference through which it is accelerated and might be expressed in joules, for example. However, it is more conventional to express the energy of a single electron in eV or keV respectively. This is the energy acquired by a single electron accelerated through a voltage (or potential difference) equal to V . In the cold cathode, there is a complicated potential distribution and not all electrons are accelerated through the full potential difference, V . Many have lower energies. Also, if the power supply has an internal ballast resistor,

the actual voltage at the cathode will be less than that at the output of the high voltage supply and it is important that the circuit have a voltage meter which indicates the true voltage at the cathode.

The beam current is the electronic charge per unit time that the beam carries to the sample. It is proportional to the number of electrons per unit time in the beam and is usually expressed in microamperes (μA) or milliamperes (mA) (these units of beam current are sometimes confused and have been incorrectly stated in several articles in the literature.) Beam current is relatively easy to monitor in the heated cathode systems, e.g., with a Faraday cup mounted in place of the sample. It is more difficult to measure beam current in the cold cathode systems. A simple Faraday cup at the sample location will not suffice because of the plasma environment; a simple Faraday cup cannot distinguish between low and high energy electrons and ions. For either hot cathode or cold cathode instruments, a simple measurement of the current in the high or low voltage leads from the power supply to the electron gun is only a first approximation to the true beam current because this provides only total current and does not indicate what portion is intercepted by apertures, lost by collision with residual gas molecules, etc. In every case, the actual beam current to the specimen is less than the output current indicated on the power supply meter.

The power in the beam is the product of the beam voltage and the beam current and is expressed in watts (volt-amperes) when, for example, the voltage is expressed in kV and the beam current is expressed in mA. Most of the power in the beam is absorbed by the target (sample) but some is intercepted by apertures. Beam power is an important parameter that determines sample heating. It is important to note that a high beam voltage by itself does not indicate high power. A high beam voltage and a low beam current may actually represent a low beam power level and therefore may not cause appreciable heating. But a high beam voltage and a high beam current occurring simultaneously will represent high power and the possibility of appreciable sample heating. Typical powers used in cold cathode systems are between 0.5 and 10 watts.

But even beam power is not the final determinant in sample heating because the power may be distributed over a relatively large area in an unfocused or defocused beam. The most critical parameter of all is **beam power density**. Beam power density is the beam power per unit area. As the value of this quantity increases, the heating (localized) caused by the beam increases. One must always avoid operating conditions which lead towards excessive heating or even incandescence of the sample. Even when not readily visible to the operator, this can produce a false red component when the CL emission spectra is analyzed and heating can also change the inherent CL characteristics of the sample.

Beam power density also determines the CL intensity per unit area. The available beam power density is not a limit to the attainable CL intensity for any of the

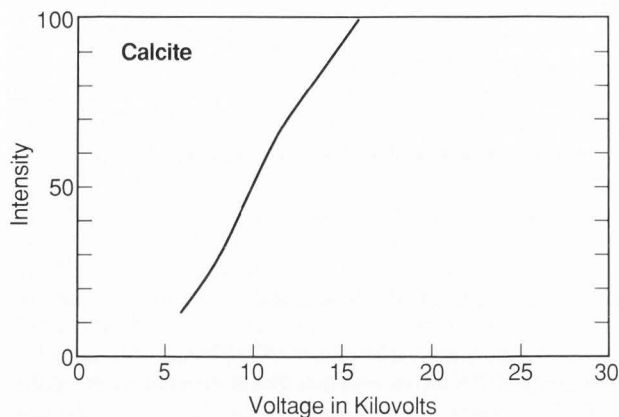


Figure 8. Variation of CL intensity of calcite (measured with a spectrophotometer set at the peak maximum) as beam energy is varied at constant beam current (by the author). Intensity scale is in arbitrary units.

instruments with beam focusing capability; usually the beam power density available is much greater than can actually be utilized.

As noted earlier, the CL intensity will increase with beam voltage (and current) for most minerals. A typical curve showing the relationship between CL intensity and beam voltage for calcite is shown in Figure 8. A similar curve applies to feldspars and to some quartz.

Some samples of quartz, and several other minerals, show a phenomenon of transient CL and under excessive bombardment the CL may change in both color and intensity. Ramseyer *et al.* (1989) have carefully studied this; their results, presented in Figure 9, show that the most favorable conditions for study of quartz CL (for quartz samples) are a beam energy of 25-30 keV and a current density of 0.4-0.5 $\mu\text{A}/\text{mm}^2$. This is a power density of 0.01-0.015 watts/mm^2 .

For a cold cathode CMA, with a 0.5 mA, 20 kV electron beam focused into a 1 mm diameter spot, the power density is about 10 watts/mm^2 , much higher than optimum. However, if this same instrument is operated at a beam current of 0.1 mA and the beam is defocused to a 1 cm diameter spot, then the power density is only about 0.02 watts/mm^2 , almost equivalent to the optimum condition of Ramseyer *et al.* (1989). In actual practice, for some samples, the operator of the CMA must sometimes defocus the beam and reduce beam current, both to prevent slide damage and also to prevent alteration of CL properties.

Beam current regulation in hot cathode and cold cathode electron guns

Beam current regulation systems are straight-forward to design for hot cathode electron guns and various feedback circuits are available which vary either the filament heating current or the potential on a control grid to keep the beam current constant.

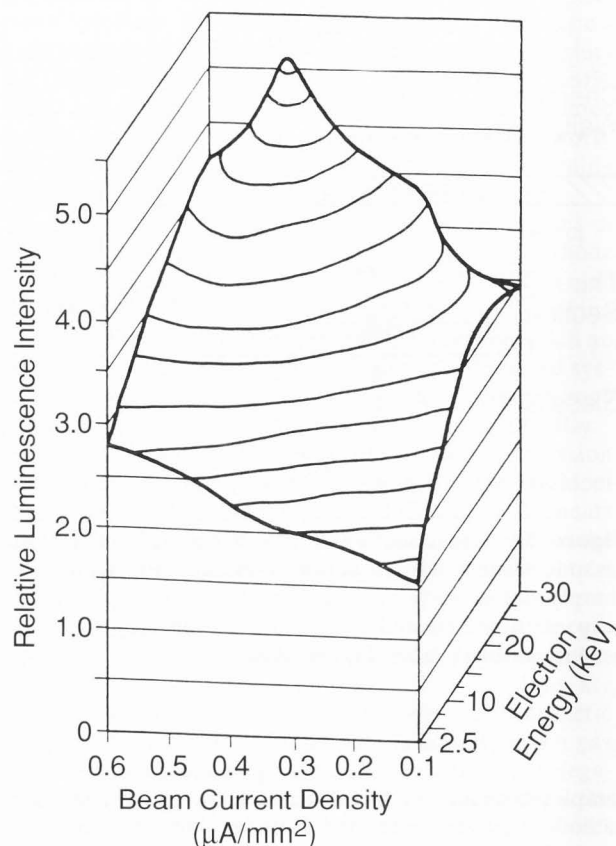


Figure 9. The variation of quartz CL with incident beam voltage and current density. (from Ramseyer *et al.* 1989)

In contrast, one of the drawbacks to the early cold cathode systems was the difficulty of adjusting and regulating the electron beam current. For a given beam energy, beam current is a function of chamber/gun pressure. In the usual region of operation, beam current decreases with pressure (Figure 10). A sensitive leak valve is normally used to adjust (increase) the pressure, after the system is pumped to an initial low pressure.

The pressure in the cold cathode system depends on several factors as indicated in Figure 11. In a well-designed vacuum system, all of these factors can be neglected except sample outgassing and the intentional leak. Until recently, manual adjustment of the intentional leak (leak valve) or adjustment of the valve in the pumping line has been the method used to adjust the system pressure and hence the beam current. This has minor disadvantages because the adjustments must be made frequently and can sometimes be difficult to do with gassy samples.

More recently, it has become feasible to replace the manual leak valve with a solenoid-controlled leak valve and use a beam current sense/feedback control system to automatically control the current (Marshall *et al.*,

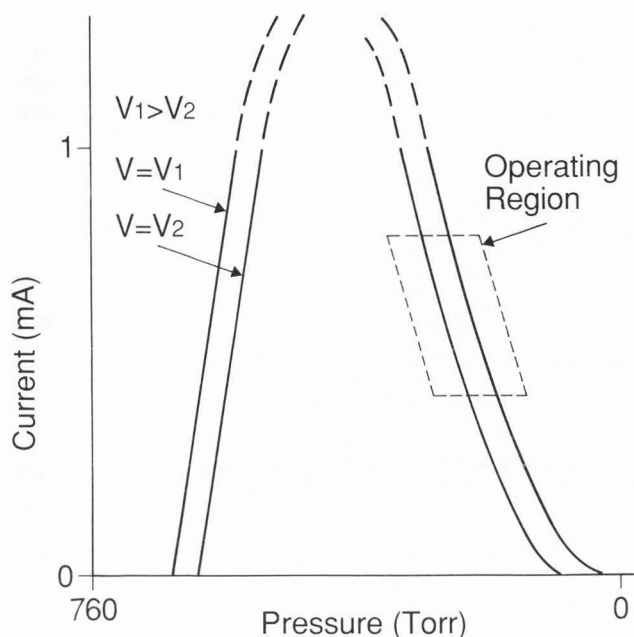


Figure 10. The generalized variation of electron current with pressure in a cold cathode discharge for two values of the voltage difference, V , between the electrodes. For the value of pressure at the maximum of this curve, discharge conditions are optimum for complete electrical breakdown and the current drawn will be at the limit of the power supply. At higher and lower pressures, the discharge will still form and the beam current will vary smoothly with pressure but in opposite directions, depending on whether it is above or below the breakdown pressure.

1990). This system, for most samples, can regulate the current to within about 1% which is much better than usually needed.

The ability to regulate the beam current automatically has proven to be an important advance. For photography of weakly-luminescing specimens, the beam must be incident on the sample for relatively long times, 1 to 2 minutes or more, and it may be tedious to manually adjust the beam current for these long exposures. For those spectrophotometer systems where the wavelength range is scanned, 2 to 3 minutes may be required to complete the scan and it is best if the entire spectrum is recorded at the same beam conditions. In both of these instances, the regulated beam frees the operator from the frequent attention required to readjust a leak valve and provides at least an order of magnitude better regulation than a human operator can provide.

Cooled Stage

One of the more recent developments is the addition of cooled stage capabilities to the cold cathode CMA systems. It is, of course, well known that the intensity of CL of some minerals increases dramatically as

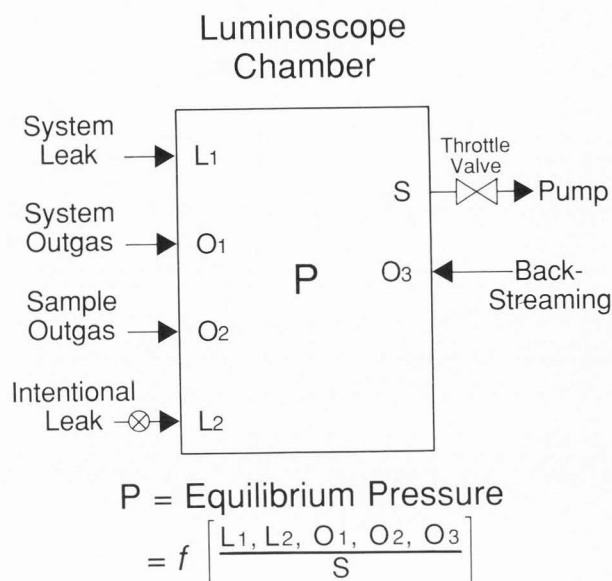


Figure 11. The sources of gas inside a typical CMA vacuum chamber. S represents the pumping speed of the pump. L and O represent leaks and sources of outgassing. The relative importance of the various sources can vary widely and in particular an attempt is made to make L_1 , O_1 and O_3 as small as possible.

the temperature of the sample is lowered and quartz is one of the best examples (Hanusiak, 1975; Marshall, 1980).

A copper block with circulating liquid nitrogen can be mounted in the CMA chamber and the thin section rests directly on this block (Figure 12). Traversing of the specimen is still possible. The cooling contact is effective enough so that even when a beam of about 7 watts over an area of about 1 cm is incident, the sample remains effectively cooled.

CL photographs of an orthoquartzite and a sandstone (containing quartz, feldspar and calcite), taken with the cooled stage under identical beam and photographic conditions show a dramatic increase in the intensity of the quartz CL but the CL of the feldspar and calcite are essentially unchanged (see color plates 6c, 6d in Marshall, 1988). This difference in the variation of the CL properties of different minerals with temperature has been discussed by Walker *et al.* (1989, 1991).

An important question which remains is whether the details of secondary quartz overgrowths, fracture fillings, and other features revealed with CL at room temperature, can still be distinguished at low temperatures or whether cooling homogenizes the CL. CL studies done on the SEM indicate that the differences remain and work is now being done with the cold cathode CMA type of instrument to confirm this.

Operation at low temperatures has also been a useful tool in studies of diamonds. The visual CL may

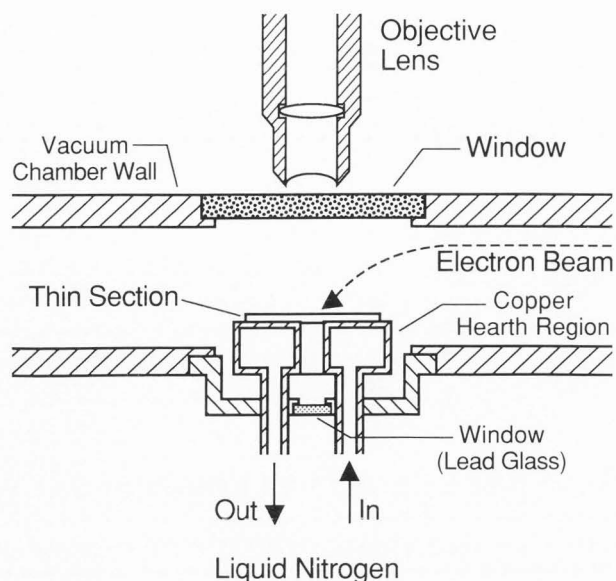


Figure 12. Cross-section of the Luminoscope chamber, fitted with a cooled stage. The sample sits on the cooled block but is still traversable by being pushed on the edges by the internal tray mechanism.

change dramatically between room temperature and low temperature (about 90°K) and CL spectra measurements at this temperature have revealed a new vibronic system (Burns *et al.*, 1990).

Energy Dispersive Spectroscopy (EDS)

The energy of the electrons in the CMAs is sufficient to produce a significant number of X-rays when the electrons interact with the sample. Marshall *et al.* (1987, 1989) fitted an EDS detector to the Luminoscope chamber enabling the user to obtain an EDS spectrum from the same area that is being viewed on the microscope (Figures 13 and 14). The detector arrangement is such that the normal CL and transmitted light viewing capabilities are not compromised.

Sometimes EDS studies are combined with CL studies but in other cases the cold cathode electron beam source is simply being used as an inexpensive, rugged, source of electrons which can be used with uncoated samples for conventional EDS analysis of various materials including both conductors and non-conductors and organic materials such as peat.

The mounting and use of the EDS detector is routine except that the electron beam intensities on the Luminoscope are sufficiently high that the X-ray beam must actually be collimated to prevent overloading of the detector electronics. EDS X-ray spectra can routinely be accumulated in 10 to 20 seconds or less.

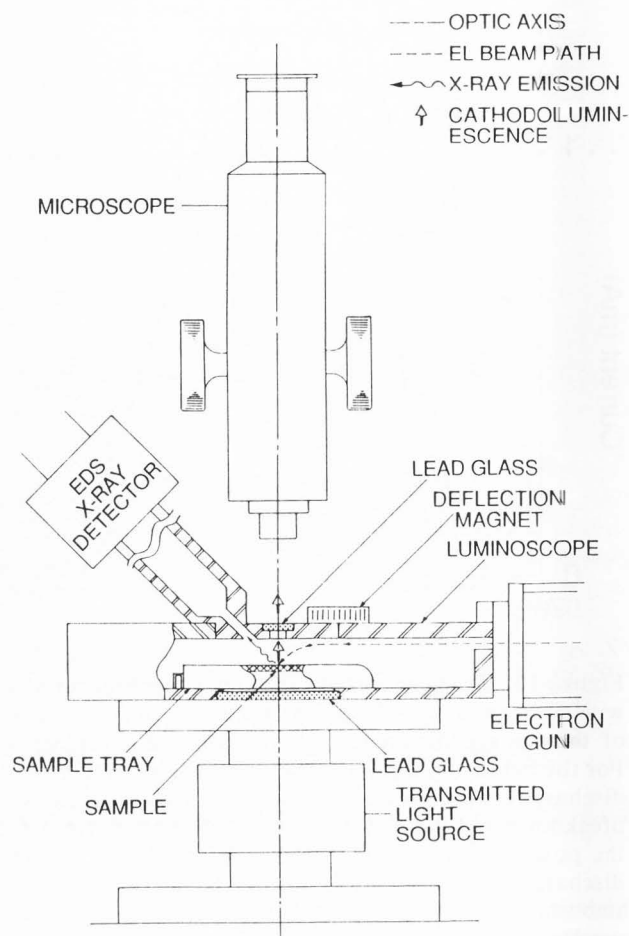


Figure 13. Arrangement of the EDS detector on the Luminoscope. Not shown is the liquid nitrogen dewar which is rigidly connected to the EDS detector. The only change made to the standard Luminoscope is to replace the standard top window with a smaller diameter window. The X-ray take-off angle is fixed at 45° for flat specimens. (From Marshall *et al.* 1987).

EDS detectors do require a supply of liquid nitrogen during operation but the consumption rate is low and if they are not being used for extended periods of time, they can be allowed to come to room temperature if the power is off.

The significant advantage of doing elemental analysis using EDS on the CMA is that conductive coatings are not needed. One can introduce and study directly thin sections and loose grains or chips and also soil, peat, ceramics, and glass, all without adding a conductive coating. Because of this feature, a ceramic streak plate, a commonly available item in the mineralogical laboratory, can be a useful sampling device for sampling some types of large or precious objects. Rather than introducing a fragment of the mineral or other item, one can simply make a streak of the sample on the streak plate and then analyze the streak. An example is shown

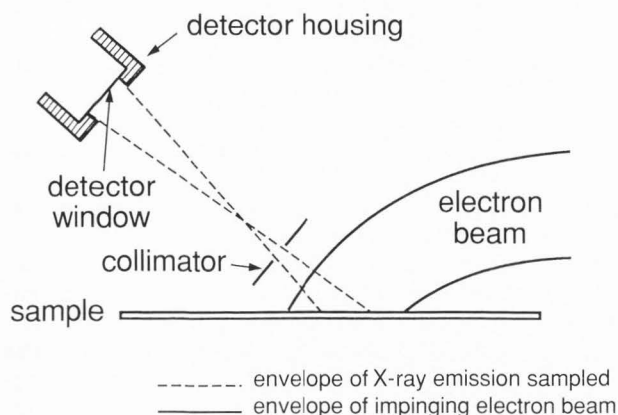


Figure 14. Detailed view of the electron beam and X-ray detector geometry. The electron beam illuminates a larger diameter spot than the collimated X-ray detector system measures. Sampled area size is defined by the collimator system, not the electron beam size.

in Figure 15 for the spectrum of a streak of sphalerite, zinc sulfide. The peaks from the streak plate appear along with the zinc and sulfur peaks and a small peak from an iron impurity.

This type of sampling is nearly non-destructive and we have used it for diverse examples. One is a finger ring, where a streak can be taken on the palm side of the ring and leaves no evidence of damage to the ring. Another is the analysis of a metal valve body where a streak can be taken with the valve remaining in place on the vacuum system, and possibly even being in operation.

Peaks from the streak plate itself (Si, Al, Na, K) must not interfere with the sample peaks. The EDS spectrum of the streak plate can be obtained separately and subtracted from the composite spectrum of the sample streak to minimize the interference. Alternatively, one could use a streak plate of a pure element though such plates are not usually so readily available as the ceramic mineralogical streak plates.

For some possible samples, e.g., a sample of Carrara marble, one can not only analyze the streak with EDS but can also observe the characteristic CL of the original marble within the streak.

Spectral Analysis of the CL Emission

Attachments for the spectral analysis of the CL emission are also an important accessory to present day CMAs. Sippel and Spencer (1970) made use of one in their work on lunar samples and their use has been discussed thoroughly by Mariano and Ring (1975) and by Mariano (1988). Wright (1991) and Steele (1991) have results on their use with SEMs and EMPAs. Ramseyer and Mullis (1990) and Walker and Burley (1991) have described spectrophotometers fitted to their hot cathode

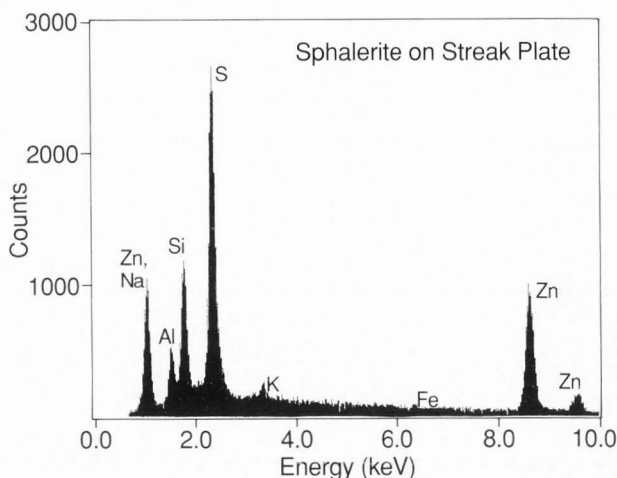


Figure 15. EDS spectrum from a streak of sphalerite (ZnS) indicating a possible small amount of Fe impurity. 18 kV; 0.06 mA; 1 cm diameter beam; 20 seconds counting time.

instruments. Remond *et al.* (1992) have presented a comprehensive review also.

With the CMA mounted on an optical microscope, one common approach is to use a special ocular with a self-contained fiber optics probe to collect a portion of the CL (Mariano and Ring, 1975). Available probes allow for collecting the CL from areas as small as 400 μm in diameter at the objective focal plane, although the available CL intensities usually restrict operation to slightly larger areas than this (700 μm in diameter or greater) unless the mineral CL is unusually bright. The corresponding area that this represents on the sample surface depends on the objective magnification. If, e.g., an objective magnification of 4X is used, then 400 μm on the objective focal plane corresponds to 100 μm on the sample surface.

An alternative means of leading the light to the spectrometer is to use a mirror and a projection lens in the light path (Owen, 1991; Ponahlo, 1992) and project the CL emission directly onto the entrance slit of the spectrometer through a lens. This method appears to provide higher transmission than the fiber optics coupling.

With either coupling system, the CL emission can be analyzed with a variety of types of spectroscopes. Most of the work to date has been done with grating monochromators equipped with a detector slit and a photomultiplier detector. More recently progress has been made with a spectrograph and array detectors which can collect the emission in part or all of the visible region simultaneously in very short times, e.g., 1-2 seconds (Owen, 1991). This feature is quite important because many important geological samples exhibit transient CL and considerable fading of the CL emission from this type of sample will take place during a conventional

spectrometer scan of 1 or 2 minutes duration (Marshall, 1988).

The background signal produced from the discharge in the cold cathode electron gun is not apparently a serious problem with CL emission analysis. In a simple experiment with the beam visible in the chamber and impinging on a conductive surface, the author found that the emission detected was at the background noise level.

The response characteristics (transmission and detection function) of the various spectral analysis systems and detectors can vary widely and, as mentioned in an earlier section, there is a clear need for standards. The SLMS standards program is addressing this problem. Mariano (1988) provides numerous examples of CL emission spectra and their interpretation. Remond *et al.* (1992) include an extensive discussion of spectral analysis systems and their use.

Concluding Remarks

The modern day CMA, with its cooled stage, EDS, spectrophotometer, and other accessories is a comprehensive instrumentation center, not only one in which a variety of important, interesting, research operations can be carried out but also one which can be used to introduce the student to a wide range of instrumental techniques with a relatively inexpensive investment in instrumentation. It is important to emphasize that CL by itself is not sufficient to provide the final solutions for most problems. Typically the CMA will be used for the initial observations and then selected samples will be further studied with CL emission spectroscopy and SEM or EMPA analytical techniques.

Acknowledgments

The author acknowledges the importance of continuing discussions with Dr. A. N. Mariano and C. Herzog. I also wish to acknowledge the assistance of Premier American Technologies Corporation in the preparation of the illustrations.

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Discussion with Reviewers

G. Remond: Using heated tungsten filament as an electron gun (SEMs, EMPAs, or hot cathode CL microscope) leads to monoenergetic incident electron beams. Besides the presence of ions when using a cold cathode electron gun, the electrons striking the specimen probably exhibit a broad energy distribution resulting from interactions with the gas molecules. Could the difference in the energy distribution of the incident beams be responsible for CL emission distribution changes as a function of the electron source?

Author: There is an appreciable energy distribution in the electron beam produced in the cold cathode discharge. I am unaware of any published measurements which can be used to predict the nature of this distribution, perhaps such measurements exist. To a modest extent, the use of a focused beam and a deflected beam, both of which actions depend on the electron beam energy, serves as a filter to sort out the electrons whose energy varies drastically from the average. In the course of observing samples, I have noted a few instances where, to the unaided eye, the color of the CL emission varies with the beam energy. But for most common samples, it is only an intensity variation that is observed. Careful measurements of spectra at different voltages would be a better test, however.

G. Remond: As mentioned in text, cold cathode electron guns are often operated by room air leaked in. Could the use of noble gas minimize the contamination observed on both the specimen surface and glass window in front of the objective lens?

Author: With air, the pressure in the discharge is approximately 60 millitorr and with helium the pressure is approximately 250 millitorr. Both of these pressures are, roughly, in the transition range between viscous flow and molecular flow. This means that there are a few collisions between gas molecules and contaminant molecules and there will be more collisions with helium than with air; so the use of helium gas to support the discharge may help slightly. The most effective means we have found for maintaining cleanliness is to be sure that samples themselves have no oil residues and to use a trap in the pumping line which intercepts most of the pump oil vapors.

M.R. Owen: The power density of commercial cold-cathode CMAs appears to be much higher than that of hot-cathode units. However, the beam current of CMAs is measured at the electron source and a large portion of the beam is lost in passing through the aperture. Can you estimate what portion of the indicated beam current actually makes it to the sample in a cold-cathode CMA?

Author: Certainly a portion of the beam is lost but I am not certain that it is a large portion. With the gun cover

removed, one can see the visible discharge in the discharge tube itself and one can also see where it strikes the anode aperture. Sometimes, in poorly aligned guns, a significant portion of the discharge is clearly not passing through the aperture. But in a correctly aligned gun, the discharge does pass through. In practice, replacement of the anode aperture because of damage by the beam is a very rare event. Probably after a period of use, if the gun is not cleaned and inspected, the operation may deteriorate and more of the beam will be intercepted. I do not want to speculate on the actual portion that does get through. I think that it would be an interesting measurement to make, though it is not an easy measurement because of the plasma environment. Note also that the usual hot cathode electron gun contains apertures and the same question must be asked about the percentage of the beam that actually gets to the sample in a hot cathode gun.

M.R. Owen: Your results suggest that cooling increases CL emission of silicates but not carbonates. Can you explain this?

Author: The answers to this question come from a complicated analysis of the energy level diagrams of the luminescing material. A discussion has been provided by Walker *et al.* (1989, 1991).