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# Calcium and fluorine signals in HS-LEIS for CaF<sub>2</sub>(111) and powder – Quantification of atomic surface concentrations using LiF(001), Ca and Cu references

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The powder of CaF<sub>2</sub> has been proposed as a practical reference for the quantitation of Ca and F in LEIS analysis. It is chemically inert, easy to clean and inexpensive. LEIS is extremely surface sensitive. Thus, in contrast to surface analytic techniques such as XPS and SIMS, the surface termination of a sample is clearly reflected in the LEIS results. It is thus unlikely that in LEIS the F/Ca ratio for CaF<sub>2</sub> is 2.0. This paper supports the reliability of the CaF<sub>2</sub> powder reference by evaluating the calcium and fluorine atomic surface concentrations, roughness factor and shows that the surface termination of the powder is the same as that of CaF<sub>2</sub>(111). The CaF<sub>2</sub> samples are treated by annealing at 725 K and measured at 625 K. The presented spectra are practically free of contamination.

Ion scattering by LiF (001), an evaporated Ca layer and a Cu foil are used as basic references for Ca and F. The atomic sensitivity factors (ASF) and the relative sensitivity factors (RSF) have been determined for F, Ca and Cu (3 keV He<sup>+</sup>, 145°).

The F/Ca atomic ratio is found to be the same ( $2.3 \pm 0.1$ ) for CaF<sub>2</sub>(111) and its powder. For the powder the Ca and F signals are reduced by a factor of  $0.77 \pm 0.03$  in comparison with those for the single crystal.

**Keywords:** High-sensitivity Low Energy Ion Scattering, HS-LEIS, ISS, calcium fluoride, CaF<sub>2</sub>, lithium fluoride, LiF(001), calcium, Ca, copper, Cu.

## INTRODUCTION

The extreme surface sensitivity and relative ease of quantitation has led to a wide variety of Low Energy Ion Scattering (LEIS) applications. The fundamentals and applications are described in two recent reviews (Refs. 1, 2). Matrix effects are generally absent or relatively small in LEIS. In a recent work by Stilhano Vilas Boas et al. (Ref. 3) the matrix effects were described for some oxides. Since the ab-initio theory to quantify the atomic concentrations still falls short, an accurate quantitation generally relies on well-defined reference materials.

The quantification of the Ca and F in CaF<sub>2</sub> powder in this contribution is based on comparison of the measured signals with those received on selected reference samples (LiF, CaF<sub>2</sub>(111) and thick layers of Ca and Cu). This kind of

quantification requires the absence of the matrix effect (charge exchange processes between the projectile and a surface atom are influenced by the chemical arrangement of the surface). Matrix effects are known to become significant for (quasi-) resonant charge transfer from an atom to the He<sup>+</sup> ion and for materials with a low work function.

Strong resonances only occur when the energy defect between the initial and final states is  $\leq 5$  eV, while the transferred electron preferably (symmetry requirement) originates from a d-level. For both reasons this is not the case for F, Ca and Cu. Sasaki et al. (Ref. 4) showed a well-defined characteristic velocity in a  $1/v$  plot for He<sup>+</sup> scattering by Ca for relevant primary energy range 1 – 3 keV.

**Accession#:** 01662, 01663, 01664, 01665, 01666

**Technique:** HS-LEIS

**Host Material:** CaF<sub>2</sub>(111), CaF<sub>2</sub> powder, LiF(001), Ca thin layer, Cu poly.

**Instrument:** IONTOF, Qtac100

**Major Elements in Spectra:** Ca, F, Cu

**Minor Elements in Spectra:** O, Cl

**Published Spectra:** 5

**Spectra in Electronic Record:** 5

**Spectral Category:** reference

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The resonant neutralization (RN) becomes a relevant neutralization mechanism for materials with a low work function ( $\phi < 3$  eV). RN to the 1st excited state of the noble gas ion then becomes possible. This process will reduce the LEIS signal (Ref. 5). This is particularly important when using the relatively slow  $\text{Ne}^+$  ions for the analysis. For  $\text{CaF}_2$  the work function will be well above the 3 eV threshold. For a thick Ca layer, however, the work function is 2.9 eV, thus just at the beginning of RN. Therefore, to avoid significant influence from this process, the relatively high velocity 3 keV  $\text{He}^+$  is used for the analysis.

Powders are often preferred as a practical reference material, since possible impurities are dispersed over a large area, thus reducing their surface concentrations. However, how much are the LEIS signals reduced by the surface roughness? The powder of calcium fluoride,  $\text{CaF}_2$ , has been proposed as a “practical” reference for calcium (Ref. 6). A complication is that the composition of the outer atomic layer of a compound is generally fundamentally different from that of the atoms below the surface. Thus before calcium fluoride can be used as reference, the surface atomic concentrations of Ca and F have to be determined.

It is a combination of data measured on a  $\text{CaF}_2(111)$  single crystal and on an evaporated 10 nm thick calcium layer which provides the calibration of the LEIS signal for a single atomic layer of calcium. Based on this, the contribution of the different atomic layers to the overall (measured) LEIS signal can be determined. Finally, the surface termination of  $\text{CaF}_2$  powder and the roughness factor are both evaluated.

The fluorine surface concentration of the powder and  $\text{CaF}_2(111)$  is evaluated using a  $\text{LiF}(001)$  single crystal as reference. A copper surface is used to determine the relative sensitivity factors for fluorine and calcium and to evaluate the instrumental sensitivity.

In this contribution, all LEIS experiments are performed with 3 keV  $\text{He}^+$  ions, using a high-sensitivity LEIS instrument with a fixed scattering angle of  $145^\circ$  (Qtac100, Ref. 7). The primary beam is parallel with the surface normal.

## Experimental spectra description - basic references: Cu, Ca and $\text{LiF}(001)$

A Cu foil, a thick evaporated Ca layer on  $\text{SiO}_2$ , and a  $\text{LiF}(001)$  single crystal are used as “basic” references for Cu, Ca and F,

resp. The spectra are given in figures 01662-01, 01663-01 and 01664-01.

For Cu (Fig. 01662-01) there is just a single peak, corresponding to  $\text{He}^+$  ions backscattered by a Cu atom in the outermost surface. Since the Cu surface is easy to clean, the signal is strong, and the background is very low (Ref. 8), the quantification of the Cu signal is straightforward. Cu is, therefore, chosen as general reference for the instrumental sensitivity of the LEIS instrument.

The Ca spectrum (Fig. 01663-01) is very different from that of Cu, see also (Ref. 4). In addition to the surface peak, there is an intense tail ( $< 1900$  eV). The extrapolated low-energy onset of this tail is around 250 eV, which agrees well with the threshold for reionization in He – Ca collisions ( $\leq 200$  eV) (Ref. 9,10).

The tail thus results from  $\text{He}^+$  ions that get first neutralized upon entering the Ca sample, and get scattered back by a Ca atom at some depth. Due to the low reionization threshold of the He – Ca collision, many of these backscattered He particles are reionized before leaving the sample (in the last collision with a surface atom) and can then be detected by the electrostatic energy analyzer. The energy loss along the in- and outgoing trajectory is responsible for the large energy distribution of the backscattered  $\text{He}^+$  ions.

The intensity at energies  $> 2100$  eV results from double collisions of He with two Ca atoms. As a result of the kinematics, the maximum energy of an in-plane double collision is, for a given total scattering angle, higher than that of a single binary collision (Ref. 10). The FWHM of the Ca surface peak is surprisingly large; certainly much larger than those for Cu and F (see Spectral Features Table). This could result from unusual inelastic processes, but also from a significant contribution from  $\text{He}^+$  ions backscattered by Ca atoms in the 2<sup>nd</sup> (possibly deeper) atomic layer.

This is the consequence of very effective reionization of the He projectiles. Thus even a weak interaction with a Ca atom during the last collision before the projectile leaves the surface leads to its reionization. The effectivity of He reionization by Ca is demonstrated by the large reionization mound at the final energy range 200 – 1850 eV (see spectrum in Fig. 01663-01). The broadening of the Ca peak by contribution from the 2<sup>nd</sup> (possibly deeper) atomic layer is visible in Fig. 01663-01, where Ca peak is fitted by Gaussian function with FWHM 64 eV.

For Cu the reionization threshold is 2100 eV (Refs. 9,10), thus explaining the absence of a tail below 2100 eV. In the Cu spectrum there is a weak but noticeable signal (see enlargement in Fig. 01662-01) between 2100 and 2250 eV (due to reionized He) and around 2450 eV (due to double Cu collisions).

For Cu and Ca the atomic surface concentrations in the outer atomic layer are estimated as (Ref. 11):

$$N_i^1 = (\rho_i N_{Av} / M_i)^{2/3}, \quad (1)$$

where  $\rho_i$  is the bulk density (g/cm<sup>3</sup>),  $N_{Av}$  is Avogadro's number, and  $M_i$  is the molar mass (g/mol). Thus  $N_{Cu}^1 = 19.32 \times 10^{14}$  atoms/cm<sup>2</sup> and  $N_{Ca}^1 = 8.16 \times 10^{14}$  atoms/cm<sup>2</sup>.

The surface of LiF(001) has been widely studied (see the Review by H. Winter (Ref. 12)). The outer atomic layer contains  $12.28 \times 10^{14}$  F atoms/cm<sup>2</sup>. Before the analysis, the sample was in-situ heated for cleaning and annealing (see the specimen descriptions). LiF is an insulator at room temperature, but a good conductor at elevated temperatures (Ref. 12). Therefore, surface charging during the LEIS experiments is avoided by heating the samples at 430 K. This procedure is preferred above using an electron shower for charge compensation, since electron bombardment is known to preferentially remove the F atoms (Ref. 13).

The LiF(001) spectrum (Fig. 01664-01) shows only the F peak, since the peak (~270 eV) of the heaviest Li isotope (mass 7) is situated outside the energy range of the spectrum. Also, the peak is weak and overlapped by the large background. The intensity between 1370 eV and 1650 eV is due to double F collisions. The increase in the intensity below 700 eV is not due to backscattered He<sup>+</sup> ions, but to secondary (sputtered) ions, such as Li<sup>+</sup>. If necessary, the sputtered ions can be excluded from the spectrum by combining the energy with a flight-time analysis (Ref. 14).

### Experimental spectra description: CaF<sub>2</sub>(111) and powder

The freshly cleaved CaF<sub>2</sub> single crystal and the powder are cleaned and annealed at 725 K. Just like LiF, CaF<sub>2</sub> is an insulator at room temperature, but becomes a conductor at elevated temperatures. Therefore, charge compensation in the LEIS experiments is not necessary for analysis at 625 K, which

also avoids preferential removal of F atoms by electron bombardment (see the discussion for LiF(001)).

The LEIS spectra are given in Fig. 01665-01 and Fig. 01666-01 for the CaF<sub>2</sub> (111) surface and CaF<sub>2</sub> powder, respectively. The spectra for the (111) surface and the powder are very different. The relative height of the Ca tail /surface peak is about 3x higher for the powder than for the (111) surface. The fact that the FWHM for the F and Ca peaks are somewhat smaller than in a previous work (Ref. 6, Fig. 01566-01) may be due to the present heat treatment, which gives a cleaner surface (no oxygen contamination). It may also partially result from small differences between the Qtacs that are used at different locations.

CaF<sub>2</sub> is known to crystallize in the fluorite structure, which can be considered as a sequence of F<sup>-</sup>-Ca<sup>2+</sup>-F<sup>-</sup> triple layers stacked in the [111] direction (Ref. 15). Cleavage occurs parallel to the (111) plane, between 2 adjacent fluorine layers. For the single crystal, the ions are incident along the [111] direction, which is an open (channeling) direction. This phenomenon is well accepted in the high energy scattering and relevant for low energy scattering with modifications that reflects the differences in the scattering cross sections, for example see Ref. 16. Therefore, many He particles will penetrate into this sample without being scattered back. This explains the low intensity of the Ca tail (< 1900 eV) in Fig. 01665-01.

### Quantitation of the LEIS results

The yield of the backscattered ions being normalized to the primary ion dose is:

$$\frac{Y_i}{Q} = N_i^{vis} \cdot c \cdot R \cdot P_i^+ \cdot d\sigma_i / d\Omega, \quad (2)$$

where  $Y_i$  is the LEIS yield for the surface peak of element i, Q the primary ion dose, c is the instrumental factor taking into account the acceptance angle and the efficiency of the analyzer. The roughness factor R ( $0 < R < 1$ ) corrects the signal for losses due to surface roughness (the lower factor, the higher roughness),  $P_i^+$  is the ion fraction of the backscattered He and  $d\sigma_i / d\Omega$  is the differential cross section for scattering by atom i.

The effective number density  $N_i^{vis}$  of atoms i in the outer ( $N^1$ ), the 2<sup>nd</sup> ( $N^2$ ) and deeper atomic layers, that contribute to the

LEIS surface peak (the density of the “visible surface atoms  $i$ ”) is given by:

$$N_i^{vis} = N_i^1 + \alpha N_i^2 + \beta N_i^3 + \dots, \quad (3)$$

where  $\alpha$  is the coefficient for the signal contribution from the 2<sup>nd</sup> atomic layer.

For 3 keV He<sup>+</sup> scattering over 145° by Cu the sharp surface peak and the very low background suggest that the LEIS signal is determined by the outer atomic layer (thus for Cu the coefficient  $\alpha$  and the coefficients of the higher terms can be neglected).

The atomic sensitivity factor (ASF) for the element  $i$  is:

$$ASF_i = Y_i / (Q \cdot N_i^{vis}), \quad (4)$$

Where, for convenience,  $Y$  is taken in counts,  $Q$  in nC and  $N_i^{vis}$  in 10<sup>14</sup> atoms/cm<sup>2</sup>. The relative sensitivity factors (RSFs) are the ASFs normalized on that of Cu:

$$RSF_i = ASF_i / ASF_{Cu} \quad (5)$$

In the Spectral Features Table the ASF's and RSF's are given for the surface peaks of Cu, Ca and F.

## Calibration calcium signal

It is generally assumed that the measured surface peaks in LEIS reflect the composition of the outermost atomic layer of the surface. However, there are cases where a contribution from “deeper” atomic layers should be taken into account as well. This is the case for calcium fluoride and the evaporated calcium film. How does one determine the LEIS contribution from the deeper layers?

As mentioned above, the structure of CaF<sub>2</sub>(111) crystal is formed by a sequence of F<sup>-</sup>-Ca<sup>2+</sup>-F<sup>-</sup> triple layers stacked in the [111] direction. The surface is terminated by an F layer (the top F). The calcium layer is situated between two fluorine layers (top F layer and lower F layer). The top F layer, the Ca layer and the lower F layer each contain 7.77 x 10<sup>14</sup> atoms/cm<sup>2</sup>. The Ca and the lower F atoms are shifted laterally with respect to the atoms in the top F layer. Thus the structure of the CaF<sub>2</sub> (111) crystal is open for the incident He<sup>+</sup> ions to reach the Ca and lower F of the outer triple layer stack. Ions that are scattered back by the Ca will be partially blocked for specific azimuths

(by the top F) on their way to the ion analyzer. Since the Qtac<sup>100</sup> analyzer (that is used in this study) collects the backscattered ions for all azimuths, the partial blocking will reduce the overall Ca signal. A contribution to the Ca peak by scattering by Ca in the 2<sup>nd</sup> Ca layer (in the 2<sup>nd</sup> triple stack) is negligible, since this is screened by 3 fluorine and 1 calcium layer. The observed surface peak (Fig. 01665-01) has a Gaussian shape and a FWHM of only 64 eV. This is typical for ions that are backscattered in a single binary He-Ca collision.

The surface peak of Ca in the spectrum (Fig. 01663-01) for the 10 nm thick evaporated Ca layer has a significantly larger FWHM (79 eV) than the Ca peak for CaF<sub>2</sub>(111) (Fig. 01665-01). Also, the Gaussian shape is distorted at the low energy side by the contributions from the deeper layers. The atomic surface concentration of Ca in the outer atomic layer is according to equation 1,  $N_{Ca}^1 = 8.16 \times 10^{14}$  atoms/cm<sup>2</sup>.

If the Ca peak of the Ca sample is fitted by a Gaussian peak with no restriction to the fitting parameters, then the resulting FWHM is 79 eV and signal is 6574 cts/nC. This value contains the contribution from deeper layers and can't be assigned directly to the known concentration of Ca in the outer atomic layer. The fitting procedure can focus on the contribution from the outermost Ca layer if the FWHM is fixed at 64 eV (the width of single Ca layer peak from CaF<sub>2</sub>(111)) and optimization is restricted only to the energy region of the right (high energy) side of the Ca peak and Gaussian function (2002 to 2200 eV). The resulting signal is reduced to 5564 cts/nC and the experimental data, background and a Gaussian fit are presented in Fig. 01663-01.

In this way we can separate the contribution from the top layer and directly assign the fitted signal to the known atomic surface concentration (5564 cts/nC, FWHM 64 eV, and  $8.16 \times 10^{14}$  atoms/cm<sup>2</sup>). Thus for the Ca sample the coefficient  $\alpha$  (equation 3) is 0.181.

Now the concentration of visible Ca atoms  $N_{Ca}^{vis}$  in the CaF<sub>2</sub>(111) sample that contribute to the measured signal (3651 cts/nC) can be quantified to  $5.36 \times 10^{14}$  atoms/cm<sup>2</sup>. The value is smaller than the theoretical one for the Ca single layer ( $7.77 \times 10^{14}$  atoms/cm<sup>2</sup>). The reduction is 31% and reflects the blocking of the Ca signal by F atoms of the top F layer. Following the identical procedure the  $N_{Ca}^1$  and  $N_{Ca}^{vis}$  for Ca in the CaF<sub>2</sub> powder sample is evaluated to  $3.85 \times 10^{14}$  atoms/cm<sup>2</sup>

and  $4.23 \times 10^{14}$  atoms/cm<sup>2</sup>, respectively. The Ca signal for the top surface layer of the powder is 72% of that for CaF<sub>2</sub>(111). The total Ca signal for the powder is 79% of that for CaF<sub>2</sub>(111).

### Calibration fluorine signal

The calibration of the fluorine signal is based on the well-defined surface of the LiF(001) reference. The outer atomic layer is terminated by fluorine and contains  $12.28 \times 10^{14}$  atoms/cm<sup>2</sup>. Since the He<sup>+</sup> ions are incident along the surface normal (a channeling direction) and the energy threshold for reionization in the He – F collision is above 2000 eV (Ref. 10), the F tail has a low intensity. The F peak will result from backscattering by F atoms in the outer surface. The F peak is Gaussian and FWHM is very similar to the value for both crystal and powder CaF<sub>2</sub> samples. The evaluated fluorine atomic surface concentrations are  $12.25 \times 10^{14}$  atoms/cm<sup>2</sup> and  $9.13 \times 10^{14}$  atoms/cm<sup>2</sup>, respectively. The value for CaF<sub>2</sub>(111) is higher than the theoretical value of F concentration in the single layer ( $7.77 \times 10^{14}$  atoms/cm<sup>2</sup>) by 58%. The fluorine atoms from the lower F layer are visible to the primary beam, but the reflected projectiles are effectively blocked in specific azimuth directions by above situated Ca and F atoms and the overall contribution from lower F layer is reduced (the total of  $\beta$  in eq. 3 is 0.58). Analogous to the Ca evaluation, the fluorine signal in the powder is 74% of the F signal for CaF<sub>2</sub>(111).

Within experimental error, the ratio of the F to Ca outer surface concentration is the same for the CaF<sub>2</sub>(111) and CaF<sub>2</sub> powder:  $2.3 \pm 0.1$  and the roughness factor for the powder is  $R = 0.77 \pm 0.03$ . The roughness factor was evaluated for the powder pressed over filtration paper. Such a surface is flat and decorated by several agglomerates of powder grains.

### CaF<sub>2</sub> powder – the practical reference

The powder of calcium fluoride, CaF<sub>2</sub>, has been suggested as “practical” reference for calcium (Ref. 6). The results of the present contribution support this suggestion and provide absolute numbers for the F and Ca surface concentrations and the roughness factor for the powder. The CaF<sub>2</sub> powder samples analyzed there and in the present contribution were prepared from the same powder, but the cleaning procedure was different. Our sample was treated by annealing at elevated temperature

and measured at temperature 625 K. Thus the spectrum is free of oxygen signal and the FWHM of the F peak is a little smaller. It was found that the temperature around 600 K was sufficient to anneal possible irradiation damage caused by primary ion beam.

#### **SPECIMEN DESCRIPTION (ACCESSION # 01662)**

**Host Material:** Cu

**CAS Registry #:** 7740-50-8

**Host Material Characteristics:** homogeneous; solid; polycrystalline; conductor; metal; Other

**Chemical Name:** copper

**Source:** MTI Corporation

**Host Composition:** Cu

**Form:** foil (25  $\mu$ m thickness)

**Structure:** FCC, polycrystalline

**History & Significance:** Copper is often used as a reference in LEIS because of its strong signal and low background. Cu is also easy to clean by ion sputtering.

**As Received Condition:** Cu foil for CVD graphene growth, as received from supplier, purity 99.99%.

**Analyzed Region:** 0.5x0.5 mm<sup>2</sup>, random location

**Ex Situ Preparation/Mounting:** none, on conducting sample holder.

**In Situ Preparation:** sputtering by Ar 3 keV (fluence  $2 \times 10^{16}$  Ar atoms/cm<sup>2</sup>), Ne 3 keV (fluence  $1 \times 10^{16}$  Ne ions/cm<sup>2</sup>).

**Charge Control:** none

**Temp. During Analysis:** ~300K

**Pressure During Analysis:**  $5.5 \times 10^{-7}$  Pa

**Partial Pressure of Reactive Gases During Analysis:**  $5.7 \times 10^{-9}$  Pa

**Preanalysis Beam Exposure:** none

#### **SPECIMEN DESCRIPTION (ACCESSION # 01663)**

**Host Material:** Ca

**CAS Registry #:** 7740-70-2

**Host Material Characteristics:** homogeneous; solid; amorphous; conductor; metal; Thin Film

**Chemical Name:** calcium

**Source:** Sigma-Aldrich

**Host Composition:** Ca

**Form:** dendritic pieces

**Structure:** Ca (FCC), polycrystalline

**History & Significance:** Calcium is extremely reactive with atmospheric compounds.

**As Received Condition:** dendritic pieces in Ar atmosphere, purity 99.99%.

**Analyzed Region:** 1.0x1.0 mm<sup>2</sup>, random location

**Ex Situ Preparation/Mounting:** UHV evaporation (SiO<sub>2</sub> substrate, 4.8x10<sup>-8</sup> Pa, 0.38 nm/min, total thickness 9.5 nm), base pressure 1.5x10<sup>-8</sup> Pa. Transfer to analysis chamber under UHV.

**In Situ Preparation:** none

**Charge Control:** none

**Temp. During Analysis:** ~300K

**Pressure During Analysis:** 5.0x10<sup>-7</sup> Pa

**Partial Pressure of Reactive Gases During Analysis:** 1.1x10<sup>-8</sup> Pa

**Preanalysis Beam Exposure:** none

#### **SPECIMEN DESCRIPTION (ACCESSION # 01664)**

**Host Material:** LiF (001)

**CAS Registry #:** 7789-24-4

**Host Material Characteristics:** homogeneous; solid; single crystal; dielectric; inorganic compound; Other

**Chemical Name:** lithium fluoride

**Source:** M. Szymonski, Jagiellonian University, Poland

**Host Composition:** LiF

**Form:** single crystal

**Structure:** LiF (001), FCC

**History & Significance:** Atmospheric stable reference material for fluorine; cleaved (001).

**As Received Condition:** single crystal (001), 1x1x0.5 cm<sup>3</sup>.

**Analyzed Region:** 1.5x1.5 mm<sup>2</sup>, random location

**Ex Situ Preparation/Mounting:** cleaved (001), ex-situ mounted on conducting sample holder.

**In Situ Preparation:** Anneal at 853 K, 10 min.

**Charge Control:** none

**Temp. During Analysis:** 430 K

**Pressure During Analysis:** 1.2x10<sup>-6</sup> Pa

**Partial Pressure of Reactive Gases During Analysis:** 3.5x10<sup>-8</sup> Pa

**Preanalysis Beam Exposure:** He<sup>+</sup> 3 keV, fluence 6x10<sup>14</sup> He atoms/cm<sup>2</sup>

#### **SPECIMEN DESCRIPTION (ACCESSION # 01665)**

**Host Material:** CaF<sub>2</sub> (111)

**CAS Registry #:** 7789-75-5

**Host Material Characteristics:** homogeneous; solid; single crystal; dielectric; inorganic compound; Other

**Chemical Name:** calcium fluoride (or fluorite)

**Source:** Korth Kristalle GmbH

**Host Composition:** CaF<sub>2</sub>

**Form:** Single crystal, (111) surface

**Structure:** FCC fluorite

**History & Significance:** Atmospheric stable reference material for calcium and fluorine; cleaved (111); highly transparent from deep ultraviolet to mid infrared; epitaxy of CaF<sub>2</sub> (111) films on Si (111) for Si-based optoelectronics; nanoelectronics.

**As Received Condition:** single crystal

**Analyzed Region:** 1.5x1.5 mm<sup>2</sup>, random location

**Ex Situ Preparation/Mounting:** Ex-situ cleaved and mounted just before introduction into vacuum analysis chamber.

**In Situ Preparation:** Anneal at 725 K, 10 min.

**Charge Control:** none, conductor at 625 K

**Temp. During Analysis:** 625K

**Pressure During Analysis:** 7.4x10<sup>-7</sup> Pa

**Partial Pressure of Reactive Gases During Analysis:** 2.0x10<sup>-8</sup> Pa

**Preanalysis Beam Exposure:** He<sup>+</sup> 3 keV, fluence 6x10<sup>14</sup> He atoms/cm<sup>2</sup>.

#### **SPECIMEN DESCRIPTION (ACCESSION # 01666)**

**Host Material:** CaF<sub>2</sub>

**CAS Registry #:** 7789-75-5

**Host Material Characteristics:** homogeneous; solid; unknown crystallinity; dielectric; inorganic compound; Powder

**Chemical Name:** calcium fluoride (or fluorite)

**Source:** Alfa Aesar

**Host Composition:** CaF<sub>2</sub>

**Form:** powder

**Structure:** CaF<sub>2</sub>

**History & Significance:** Atmospheric stable reference material for calcium and fluorine.

**As Received Condition:** powder, purity 99.95%

**Analyzed Region:** 1.5x1.5 mm<sup>2</sup>, random location

**Ex Situ Preparation/Mounting:** Ex-situ pressed into a pellet of 10 mm diameter with about 500 N of force over a filtration paper.

**In Situ Preparation:** Anneal at 925 K, 10 min.

**Charge Control:** none, conductor at 625 K

**Temp. During Analysis:** 625 K

**Pressure During Analysis:** 7.4x10<sup>-7</sup> Pa

**Partial Pressure of Reactive Gases During Analysis:** 2x10<sup>-8</sup> Pa

**Preanalysis Beam Exposure:** He<sup>+</sup> 3 keV, fluence 7x10<sup>14</sup> He atoms/cm<sup>2</sup>

## INSTRUMENT DESCRIPTION

**Manufacturer and Model:** IONTOF

Qtac100

**Analyzer Type:** Double Toroidal

**Number of Detector Elements:** continuous

## INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

### ■Spectrometer

**Analyzer Mode:** constant pass energy

**Energy Dependence of Detection:** constant

**Charge Compensation Energy:** not used

**Time of Flight Filter Used :** no

**Time of Flight Filter Comment :** n/a

### ■Ion Sources

#### *Ion Source 1 of 1*

**Purpose of this Ion Source:** analysis beam

**Manufacturer and Model:** IONTOF electron impact ion source.

**Energy:** 3000 eV

**Current:**  $2\text{-}5 \times 10^{-6}$  mA

**Current Measurement Method:** Faraday cup

**Species:** 4He

**Spot Size (unrastered):**  $50 \times 50 \text{ } \mu\text{m}$

**Raster Size:** maximum  $2000 \times 2000 \text{ } \mu\text{m}$

**Incident Angle:**  $0^\circ$

**Polar Angle:** N/A

**Azimuthal Angle:**  $0\text{-}360^\circ$

**Scattering Angle:**  $145^\circ$

**Comment:** N/A

## DATA ANALYSIS METHOD

**Energy Scale Correction:** no correction

**Peak Shape and Background Method:** Gaussian + sloped error function (Ref. 6, Accession 01566-02).

**Quantitation Method:** The atomic sensitivity factors for F and Cu are determined using their known atomic concentrations in the outermost atomic layer of LiF(001) and of Cu metal. For Ca in Ca metal there is not only a signal contribution from the outermost atomic layer but also (15%) from the 2nd atomic layer.

**Sensitivity Factor (source):** relative sensitivity factors of Ca and F to polycrystalline Cu are: 0.95 and 0.16, resp.

## ACKNOWLEDGMENTS

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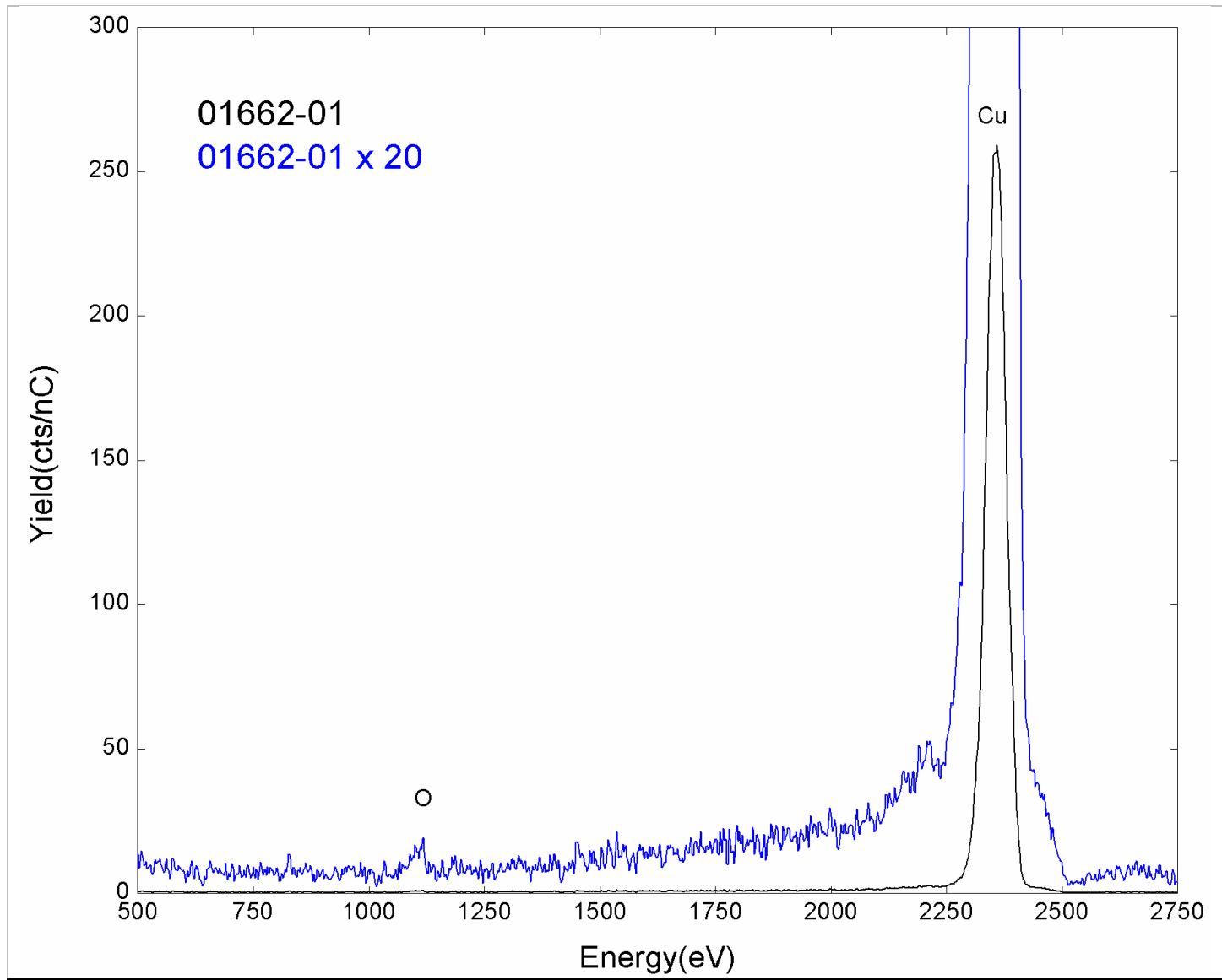
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SPECTRAL FEATURES TABLE							
Spectrum ID #	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (cts/nC)	Sensitivity Factors ASF ; RSF	Concentration (other)	Primary Ion Species	Peak Assignment
01662-01	2357	51	13901	720 ; 1.00	19.3x10 <sup>14</sup>	<sup>4</sup> He	Cu
01663-01	2012	79	6574	682 ; 0.95	9.6x10 <sup>14</sup>	<sup>4</sup> He	Ca
01663-01	2017	64	5564	682 ; 0.95	8.2x10 <sup>14</sup>	<sup>4</sup> He	Ca
01664-01	1306	52	1434	117 ; 0.16	12.3x10 <sup>14</sup>	<sup>4</sup> He	F
01665-01	1308	49	1431	117 ; 0.16	12.3x10 <sup>14</sup>	<sup>4</sup> He	F
01665-01	2030	64	3651	682 ; 0.95	5.4x10 <sup>14</sup>	<sup>4</sup> He	Ca
01666-01	1307	50	1066	117 ; 0.16	9.1x10 <sup>14</sup>	<sup>4</sup> He	F
01666-01	2025	69	2885	682 ; 0.95	4.2x10 <sup>14</sup>	<sup>4</sup> He	Ca
01666-01	2026	64	2626	682 ; 0.95	3.9x10 <sup>14</sup>	<sup>4</sup> He	Ca

**Peak comment:** The Ca peaks for Ca(10nm) and CaF<sub>2</sub> powder materials are evaluated twice. The lower evaluation uses the FWHM = 64 eV, the value fixed from Ca peak evaluation at CaF<sub>2</sub>(111), where the single layer contributes to the Ca signal.

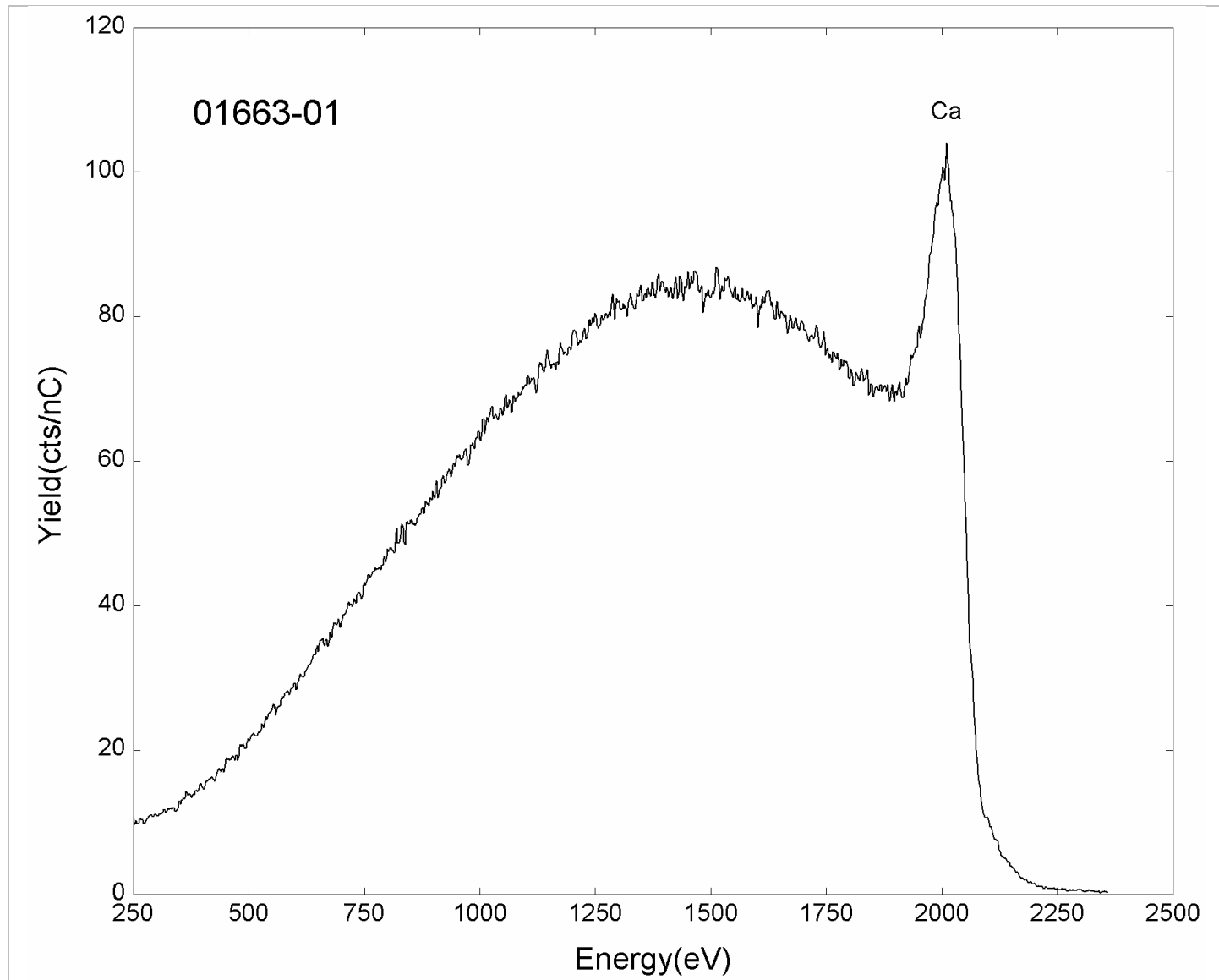
GUIDE TO FIGURES				
Spectrum ID #	Spectral Region	Multiplier	Baseline	Comment #
01662-01	500 – 2750 eV	1; 20	0	Cu poly
01663-01	250 – 2500 eV	1	0	Ca (10nm) on SiO <sub>2</sub>
01663-01	1800 – 2250 eV	1	0	Ca fit (from 01663-01)
01664-01	350 – 2000 eV	1	0	LiF(001)
01665-01	250 – 2500 eV	1	0	CaF <sub>2</sub> (111)
01666-01	250 – 2500 eV	1	0	CaF <sub>2</sub> powder

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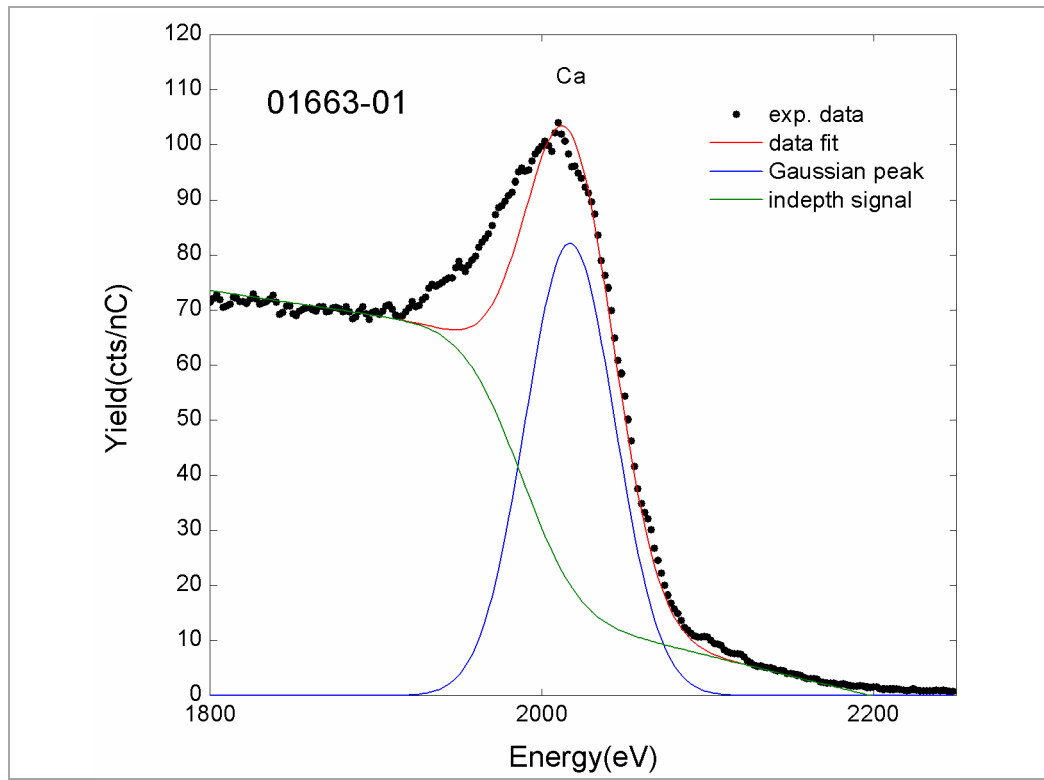
Accession #	01662-01
Host Material	Cu
Technique	HS-LEIS
Spectral Region	survey
Instrument	Qtac 100, IONTOF GmbH
Primary Beam Energy	3000 eV
Primary Ion Species	4He
Primary Ion Fluence	$8.2 \times 10^{14}$ ion/cm <sup>2</sup>
Analysis Field of View	0.5 x mm 0.5 mm
Analyzer Type	Double Toroidal
Scattering Angle	145°
Analyzer Pass Energy	3000 eV
Analyzer Resolution	1.5 %
Total Signal Accumulation Time	119 s
Total Elapsed Time	142 s
Number of Scans	5
Effective Detector Width	184 eV

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Accession #	01663-01
Host Material	Ca
Technique	HS-LEIS
Spectral Region	survey
Instrument	Qtac 100, IONTOF GmbH
Primary Beam Energy	3000 eV
Primary Ion Species	4He
Primary Ion Fluence	3.3x10 <sup>14</sup> ion/cm <sup>2</sup>
Analysis Field of View	1.0 x mm 1.0 mm
Analyzer Type	Double Toroidal
Scattering Angle	145°
Analyzer Pass Energy	3000 eV
Analyzer Resolution	1.5 %
Total Signal Accumulation Time	120 s
Total Elapsed Time	144 s
Number of Scans	5
Effective Detector Width	184 eV

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■ **Accession #:** 01663-01

■ **Host Material:** Ca thick layer on SiO<sub>2</sub>

■ **Technique:** HS-LEIS

■ **Spectral Region:** survey (Ca fit)

Instrument: Qtac 100, IONTOF GmbH

Primary Beam Energy: 3000 eV

Primary Ion Species: 4He

Primary Ion Fluence: 3.3x10<sup>14</sup> ion/cm<sup>2</sup>

Analysis Field of View: 1.0 mm x 1.0 mm

Analyzer Type: Double Toroidal

Scattering Angle 145 °

Analyzer Pass Energy 3000 eV

Analyzer Resolution: 1.5 %

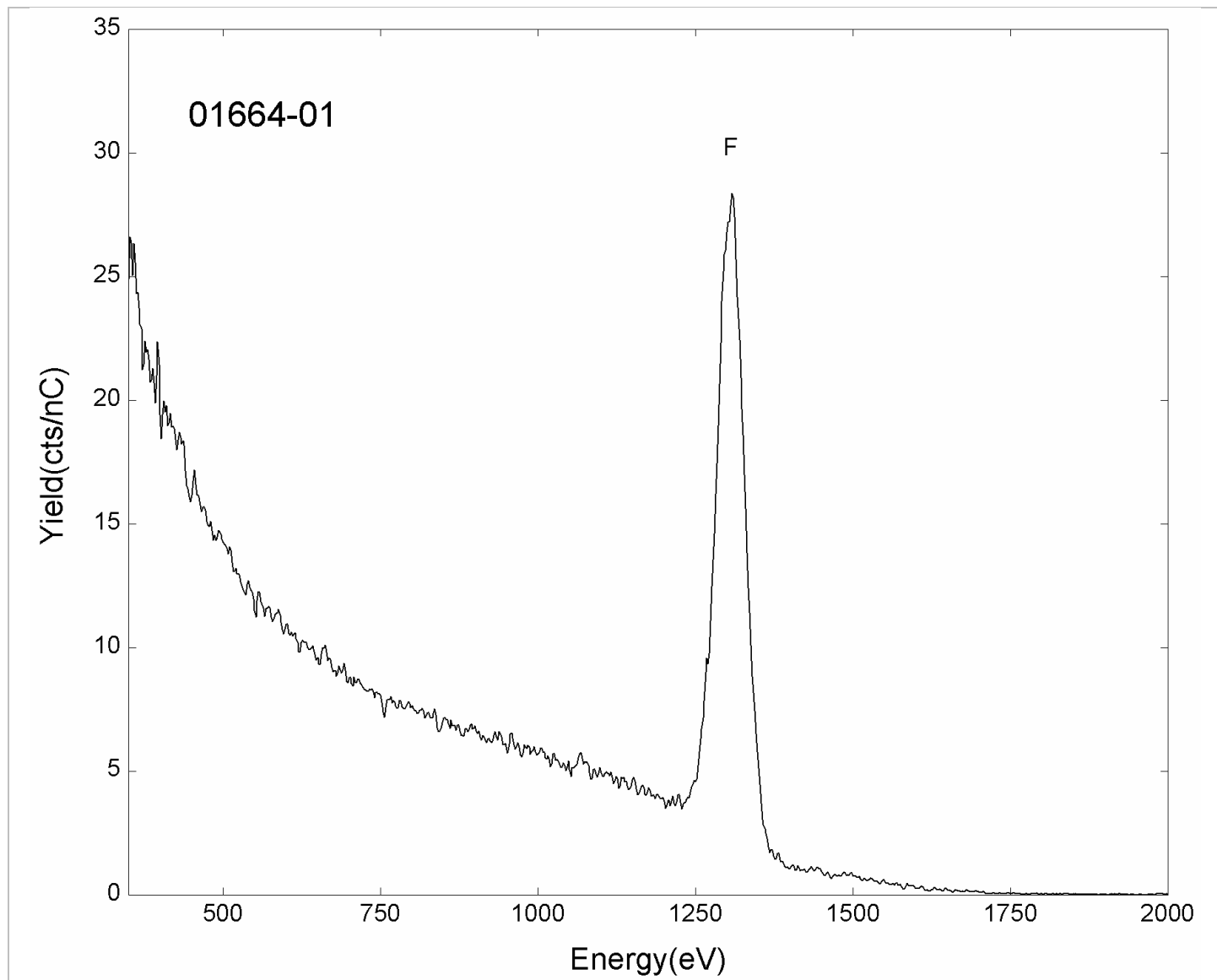
Total Signal Accumulation Time: 120 s

Total Elapsed Time: 144 s

Number of Scans: 5

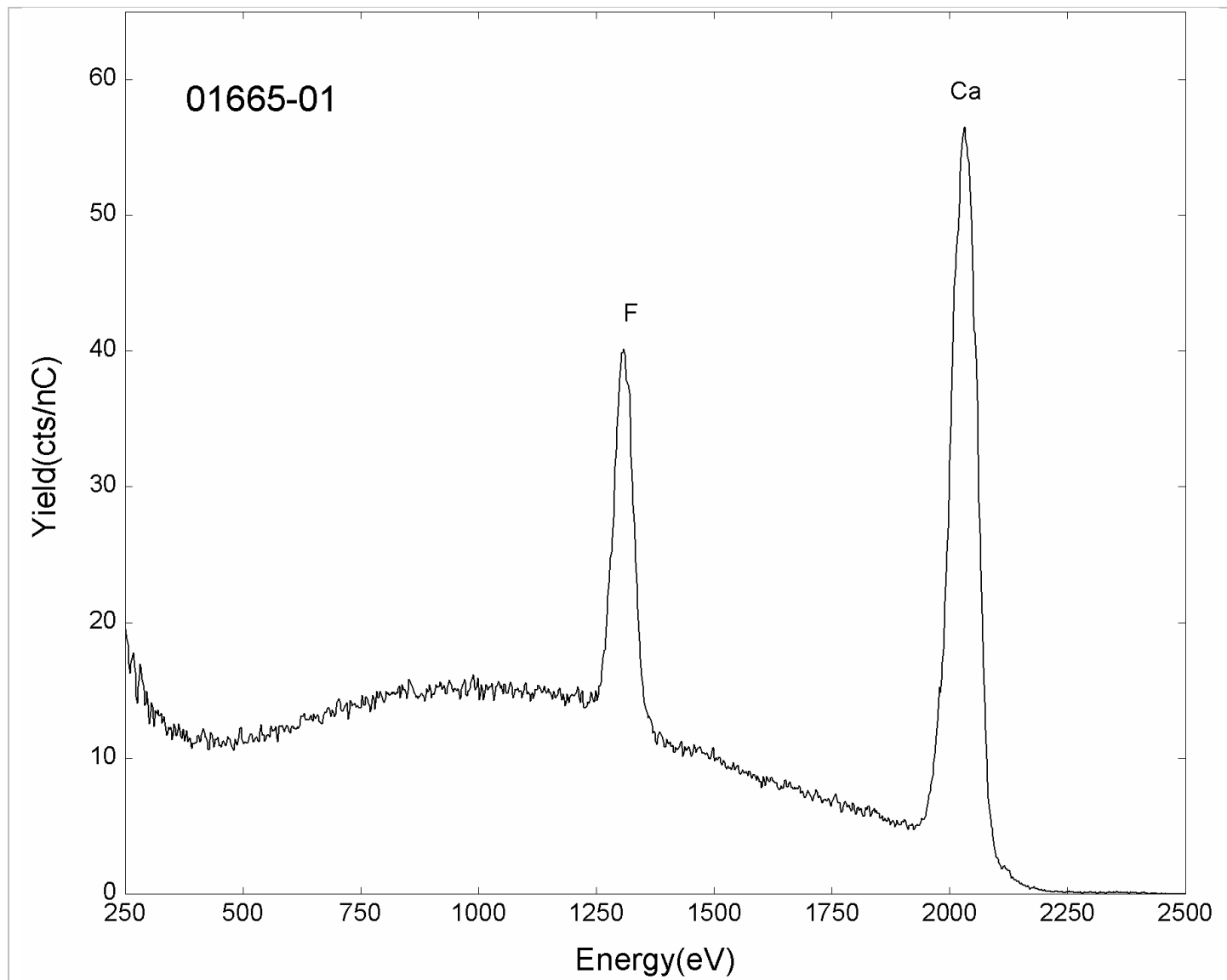
Effective Detector Width: 184 eV

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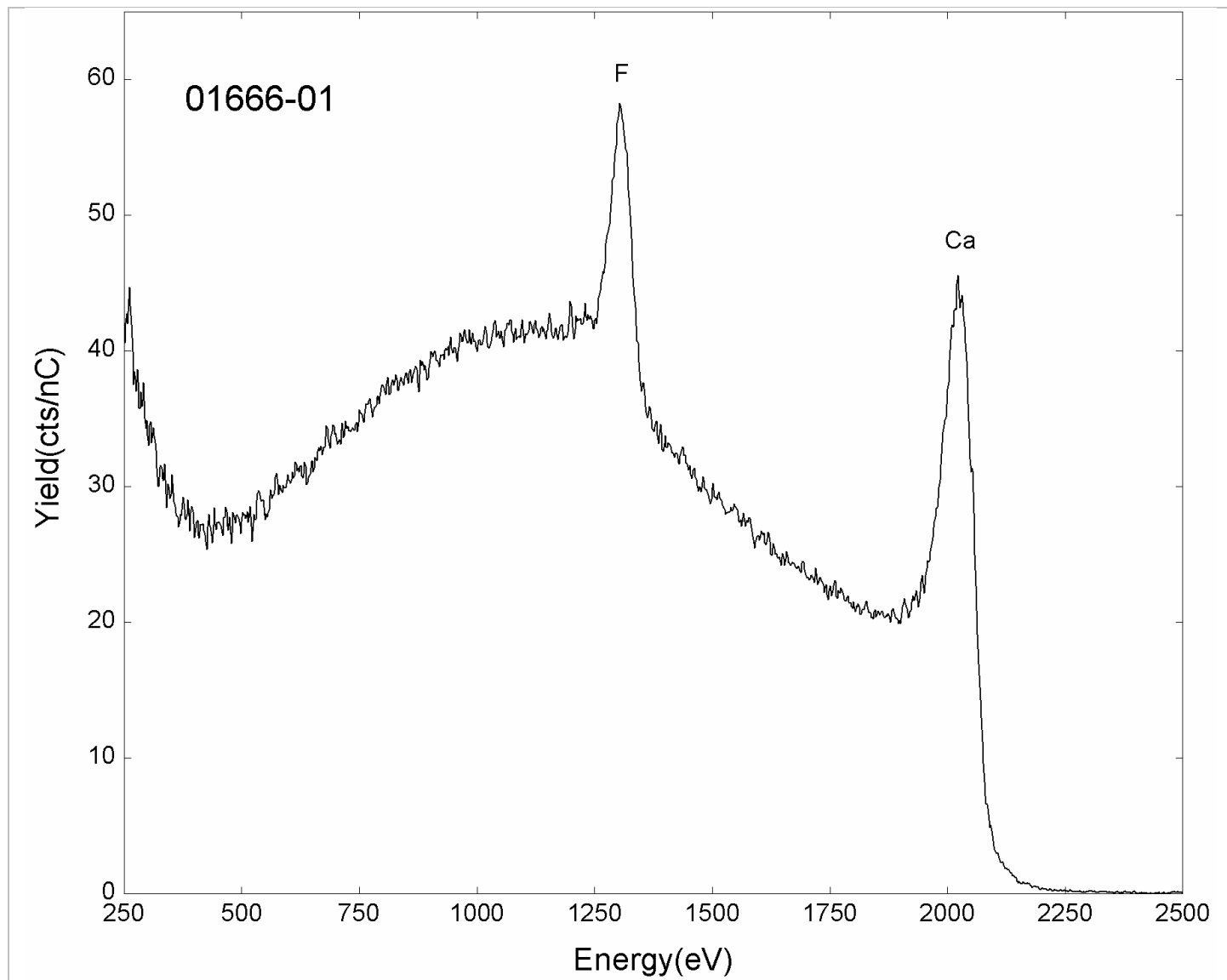
Accession #	01664-01
Host Material	LiF(001)
Technique	HS-LEIS
Spectral Region	survey
Instrument	Qtac 100, IONTOF GmbH
Primary Beam Energy	3000 eV
Primary Ion Species	4He
Primary Ion Fluence	1.4x10 <sup>14</sup> ion/cm <sup>2</sup>
Analysis Field of View	1.5 x mm 1.5 mm
Analyzer Type	Double Toroidal
Scattering Angle	145°
Analyzer Pass Energy	3000 eV
Analyzer Resolution	1.5 %
Total Signal Accumulation Time	120 s
Total Elapsed Time	145 s
Number of Scans	5
Effective Detector Width	184 eV

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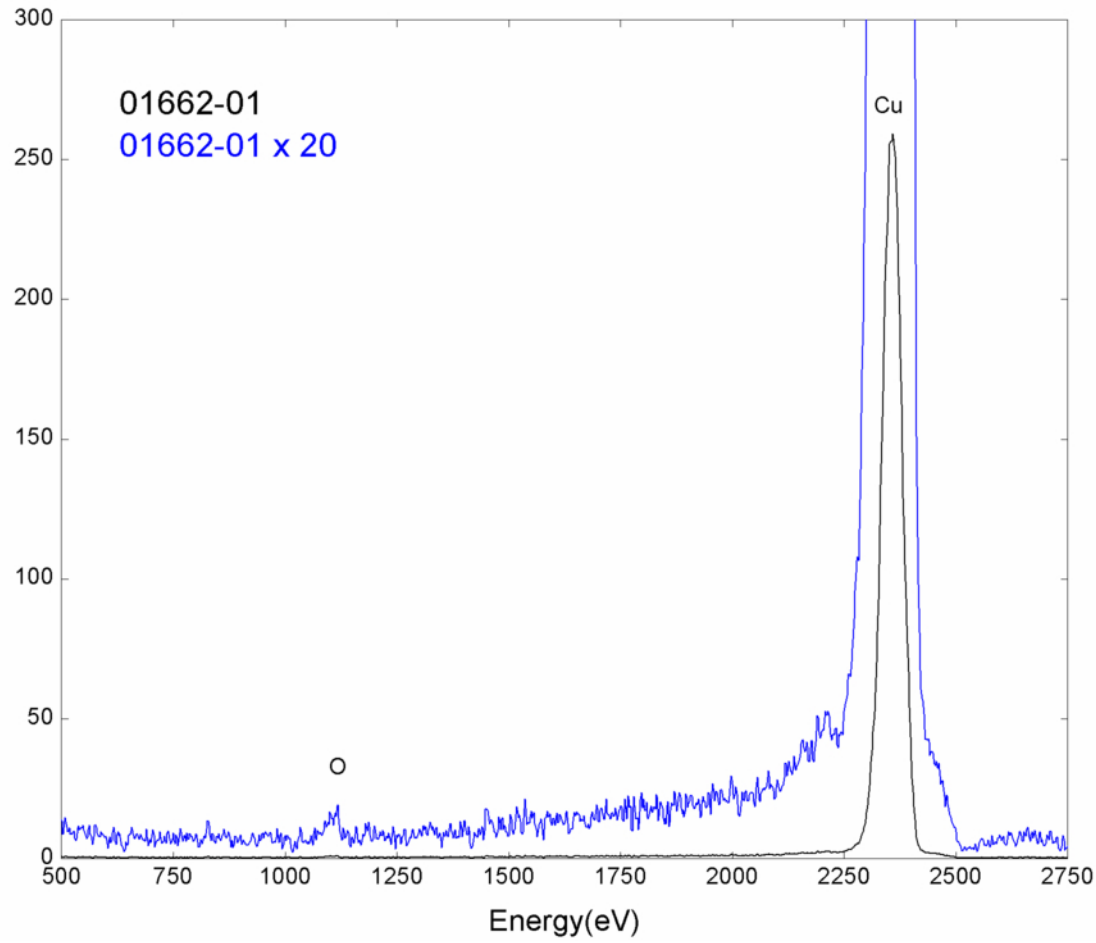
Accession #	01665-01
Host Material	CaF <sub>2</sub> (111)
Technique	HS-LEIS
Spectral Region	survey
Instrument	Qtac 100, IONTOF GmbH
Primary Beam Energy	3000 eV
Primary Ion Species	4He
Primary Ion Fluence	1.8x10 <sup>14</sup> ion/cm <sup>2</sup>
Analysis Field of View	1.5 x mm 1.5 mm
Analyzer Type	Double Toroidal
Scattering Angle	145°
Analyzer Pass Energy	3000 eV
Analyzer Resolution	1.5 %
Total Signal Accumulation Time	239 s
Total Elapsed Time	269 s
Number of Scans	5
Effective Detector Width	184 eV

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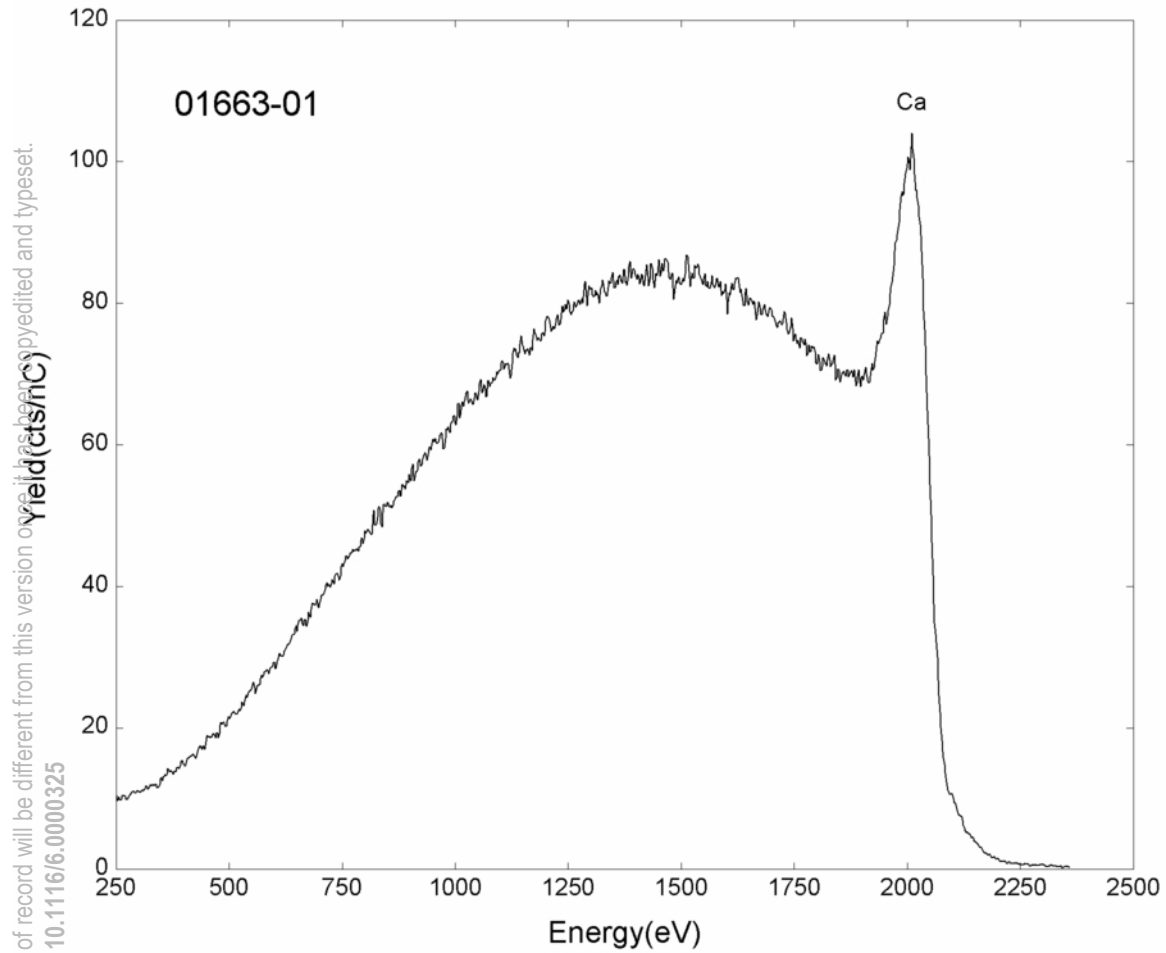
Accession #	01666-01
Host Material	CaF <sub>2</sub> powder
Technique	HS-LEIS
Spectral Region	survey
Instrument	Qtac 100, IONTOF GmbH
Primary Beam Energy	3000 eV
Primary Ion Species	<sup>4</sup> He
Primary Ion Fluence	1.8x10 <sup>14</sup> ion/cm <sup>2</sup>
Analysis Field of View	1.5 x mm 1.5 mm
Analyzer Type	Double Toroidal
Scattering Angle	145°
Analyzer Pass Energy	3000 eV
Analyzer Resolution	1.5 %
Total Signal Accumulation Time	240 s
Total Elapsed Time	279 s
Number of Scans	5
Effective Detector Width	184 eV

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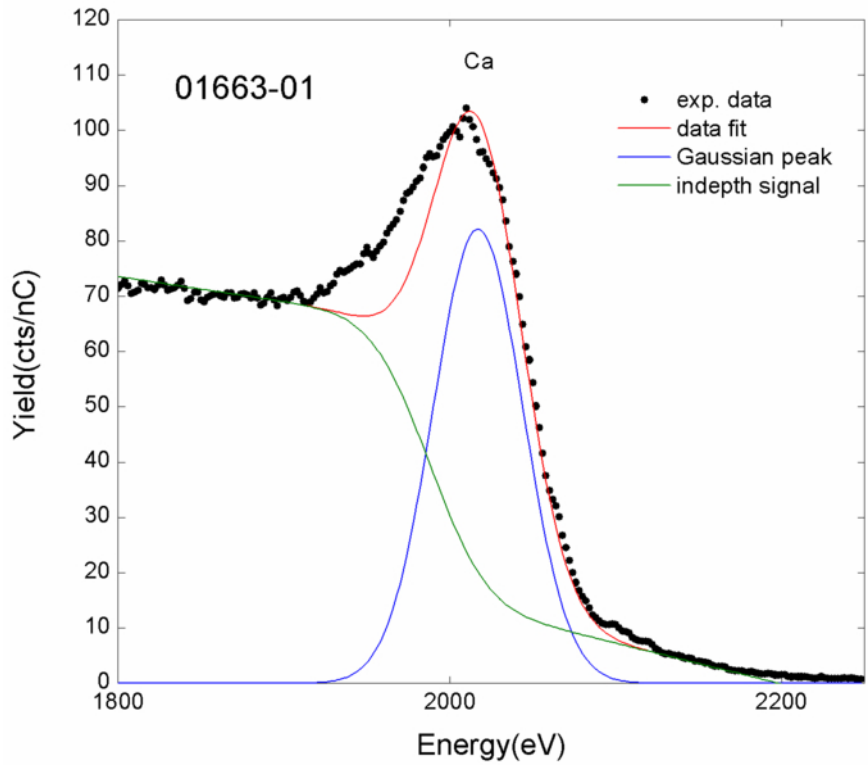


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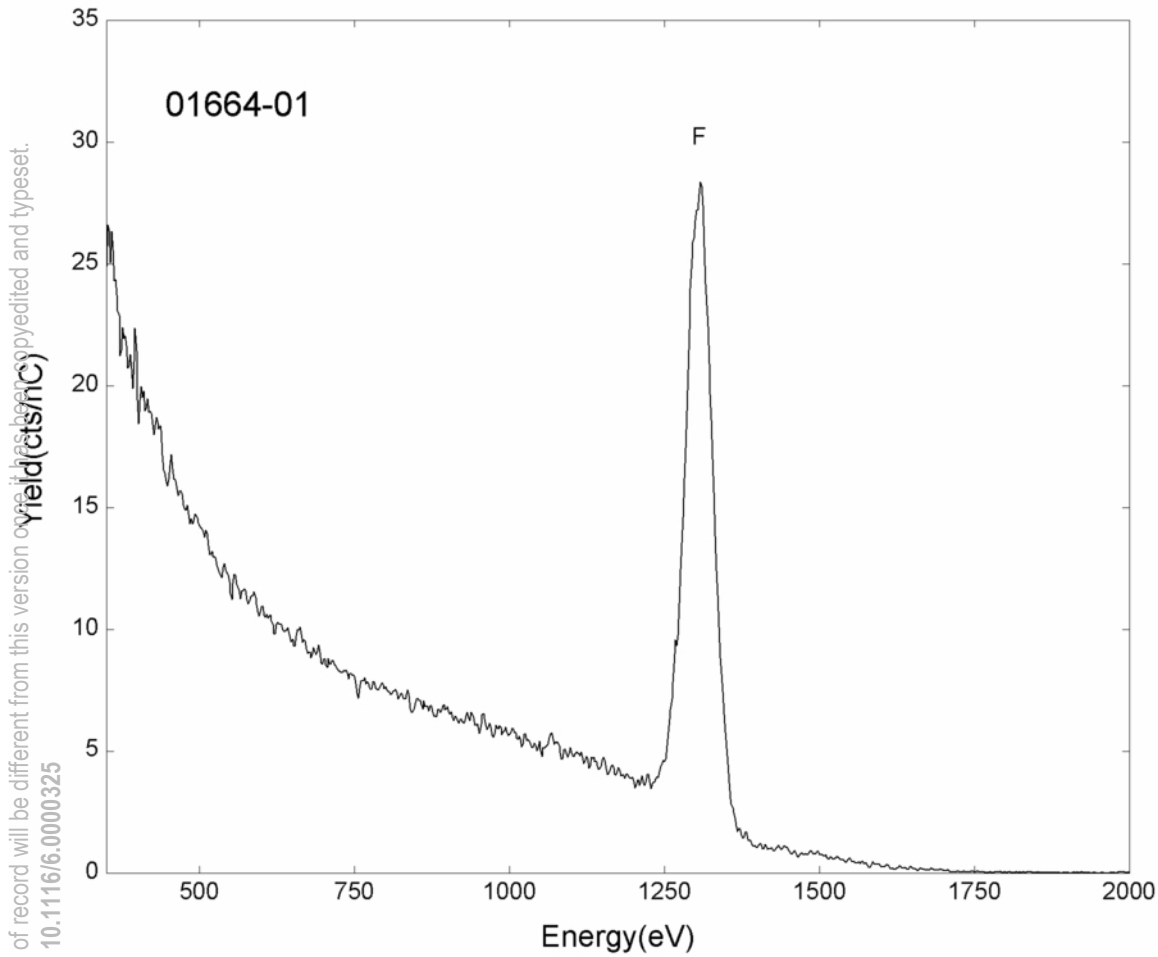
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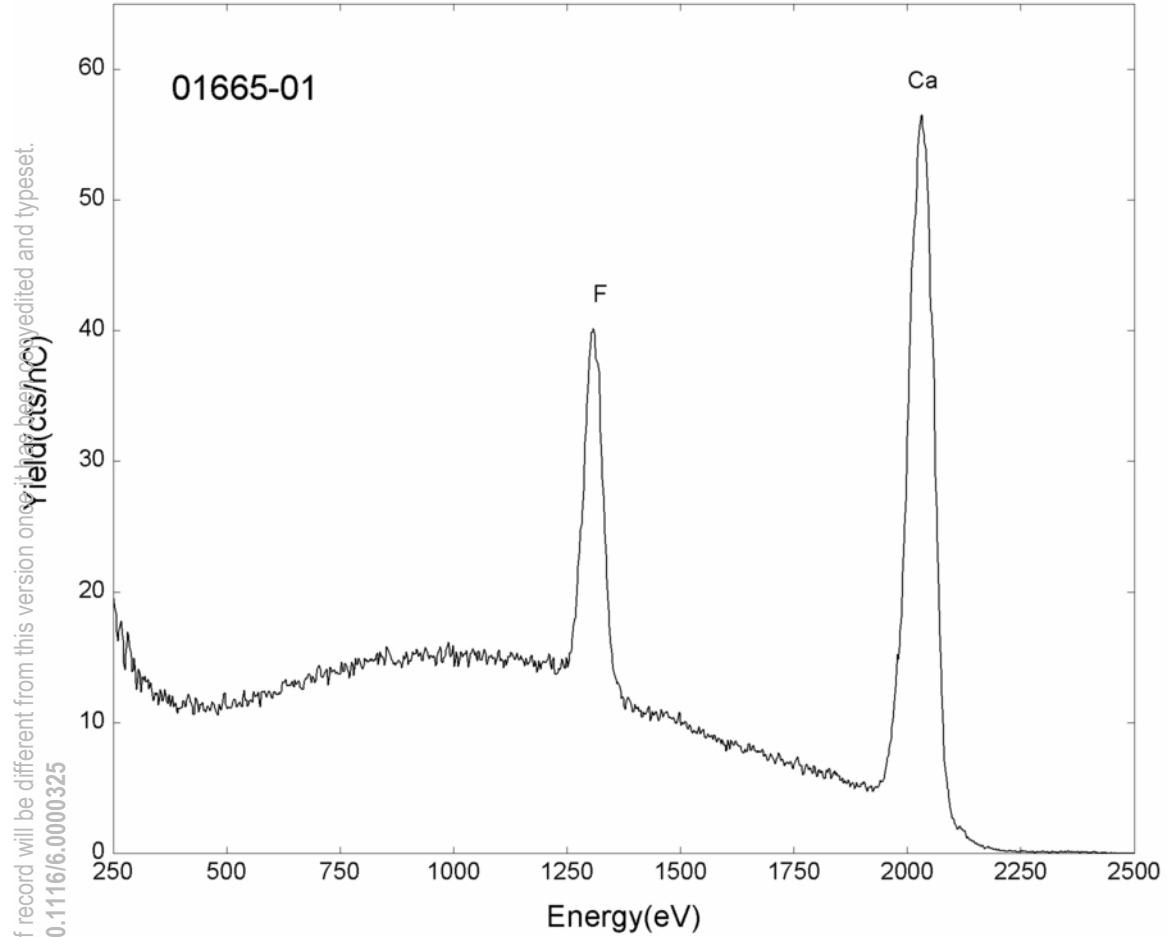


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