

GN
MEBA



GROUPEMENT NATIONAL DE
MICROSCOPIE ELECTRONIQUE A BALAYAGE
ET DE MICROANALYSES



En convention de coopération avec la Société Française de Physique

jours thématiques

« MEB - Matériaux naturels et Environnement »

12 et 13 juin 2014

BRGM (Bureau de Recherche Géologique et Minière) à Orléans (45)

Cartographie élémentaire à la microsonde électronique des mineurs et traces pour comprendre l'histoire de cristallisation des roches métamorphiques

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ISTeP



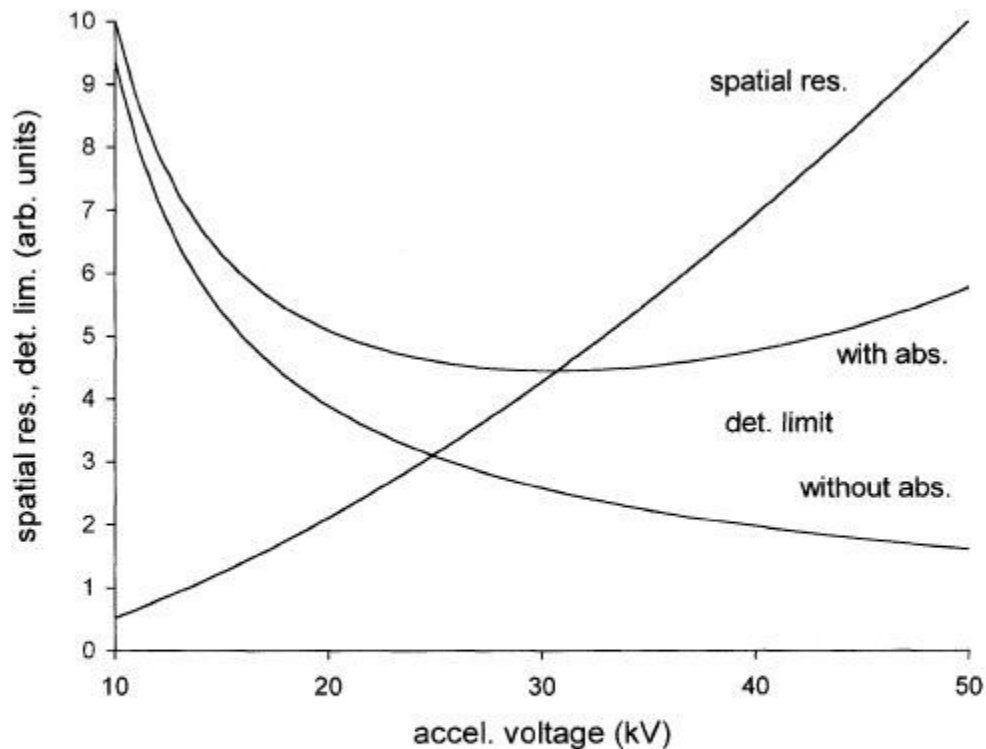


Fig. 1. Calculated relative spatial resolution and detection limit as function of accelerating voltage; detection limit shown with and without absorption in the sample (assuming arbitrary values of mass absorption coefficients for illustrative purposes)

Trace element analysis benefits equally from maximisation of peak intensity and peak-to-background ratio, both of which increase with increasing accelerating voltage (V_0), though in cases of high absorption the peak intensity passes through a maximum and then decreases owing to the increasing depth of X-ray production. However, electron penetration increases approximately as $V_0^{5/3}$, with a consequent worsening of spatial resolution.

LIMITE DE DETECTION

La plus faible concentration qui peut être détectée avec un certain niveau de confiance

Limite au-delà de laquelle on distingue une raie caractéristique du fond continu

METHODE DITE DES 3 SIGMAS :

raie caractéristique détectable :

Int. Raie $> 3 \times$ fluctuations stat. du FC
 $3 \times \sigma$ des valeurs de l'int. du FC

ESTIMATION DE LA LIMITE DE DETECTION

échantillon: $I = I_e - B_e$

- écart-type de la différence de deux intensités :

$$\sigma = \sqrt{I_e / t_e + B_e / \alpha_e \cdot t_e} = \sqrt{\frac{B_e}{t_e} \cdot \left(1 + \frac{1}{\alpha_e}\right)} = \sqrt{2} \cdot \sqrt{\frac{B_e}{t_e}}$$

avec $I_e = B_e$, $\alpha_e = 1$

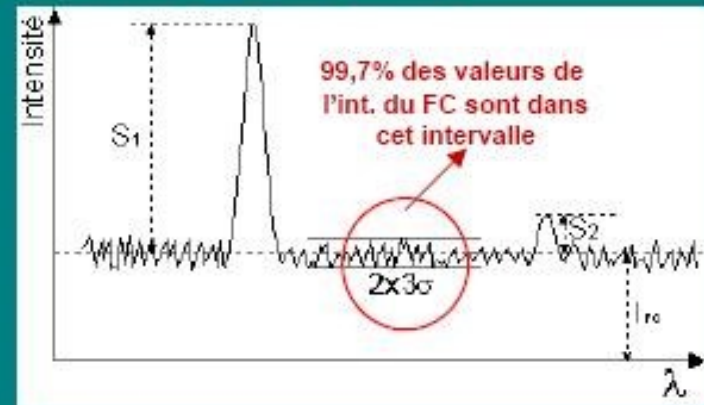
$$I_{\text{limite détectée}} = 3\sigma$$

- estimation de la concentration minimum détectable :

$$C_L = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot I_{\text{limite}} = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot 3\sigma = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot 3 \cdot \sqrt{2} \cdot \sqrt{B_e / t_e}$$

C_L dépend de la nature du matériau analysé

Doc. F. Robaut



SEUIL DE DETECTION

Ancey et Tixier (1978)

A partir du test de Chi-deux sur l'estimateur de la Conc. apparente:

prise en compte des risques α et β dans la fonction λ

$$C_{\min} = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot \left(\frac{\lambda(\alpha, \beta)}{2 \cdot t_e} \right) \left(1 + \sqrt{1 + \frac{4B_e t_e (1 + 1/\alpha_e)}{\lambda(\alpha, \beta)}} \right)$$

risque $\alpha = \beta = 5\%$

Probabilité 95% : pour $\alpha = \beta = 0.05$, $\lambda(\alpha, \beta) = 13$
Probabilité 99% : pour $\alpha = \beta = 0.01$, $\lambda(\alpha, \beta) = 24.03$

$$\text{Avec : } \alpha_e = 1 : C_{\min} = \frac{C_t}{I_t - B_t} \cdot ZAF \cdot f(\alpha, \beta) \cdot \sqrt{\frac{B_e}{t_e}}$$

Pour de faibles teneurs,

$t_{\text{comptage pic}} = t_{\text{comptage FC}}$

car I_e voisin de B_e

$f(\alpha, \beta) = 5.09$ pour : $\alpha = \beta = 0.05$

$f(\alpha, \beta) = 6.93$ pour : $\alpha = \beta = 0.01$

Doc. F. Robaut

Ne pas confondre précision et justesse!!

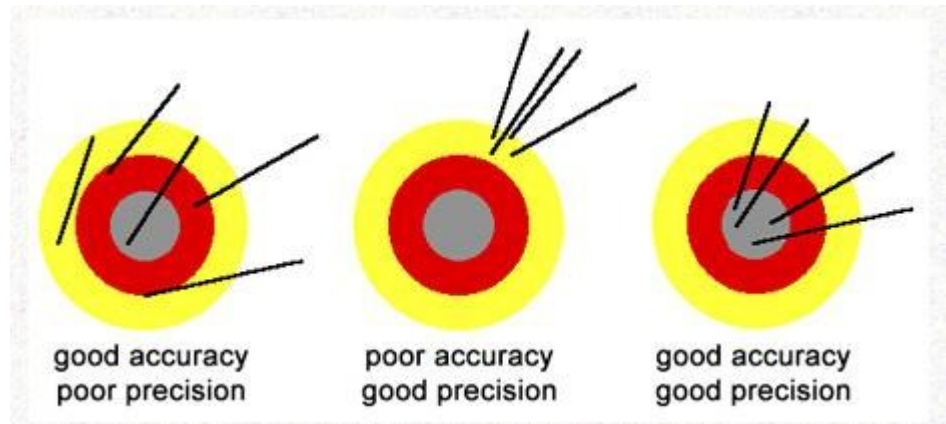
Une valeur approchée (mais souvent suffisante) de la précision peut être obtenue par la statistique de Poisson qui s'applique au cas des émissions radiatives :

Pour un comptage total N , l'écart-type s est donné par

$$s = \sqrt{N}$$

Selon le risque statistique désiré (68, 95 ou 99%), on prendra s , $2s$ ou $3s$

Une concentration peut être mesurée avec une bonne précision statistique mais être éloignée de la conc. vraie



Modélisation du fond continu

Bremsstrahlung = ralentissement des électrons incidents dans la cible
(loi de Kramer)

+

Réflexion spéculaire

Specular reflection is the mirror-like reflection of light from a surface, in which light from a single incoming direction (a ray) is reflected into a single outgoing direction.



Specular Reflection
(smooth surfaces)

+

Piémont de pic d'élément majeur

≠

Réflexion de Bragg

$$n\lambda = 2d \sin \theta.$$

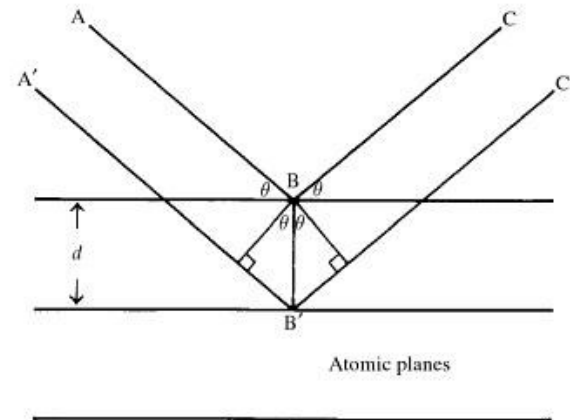
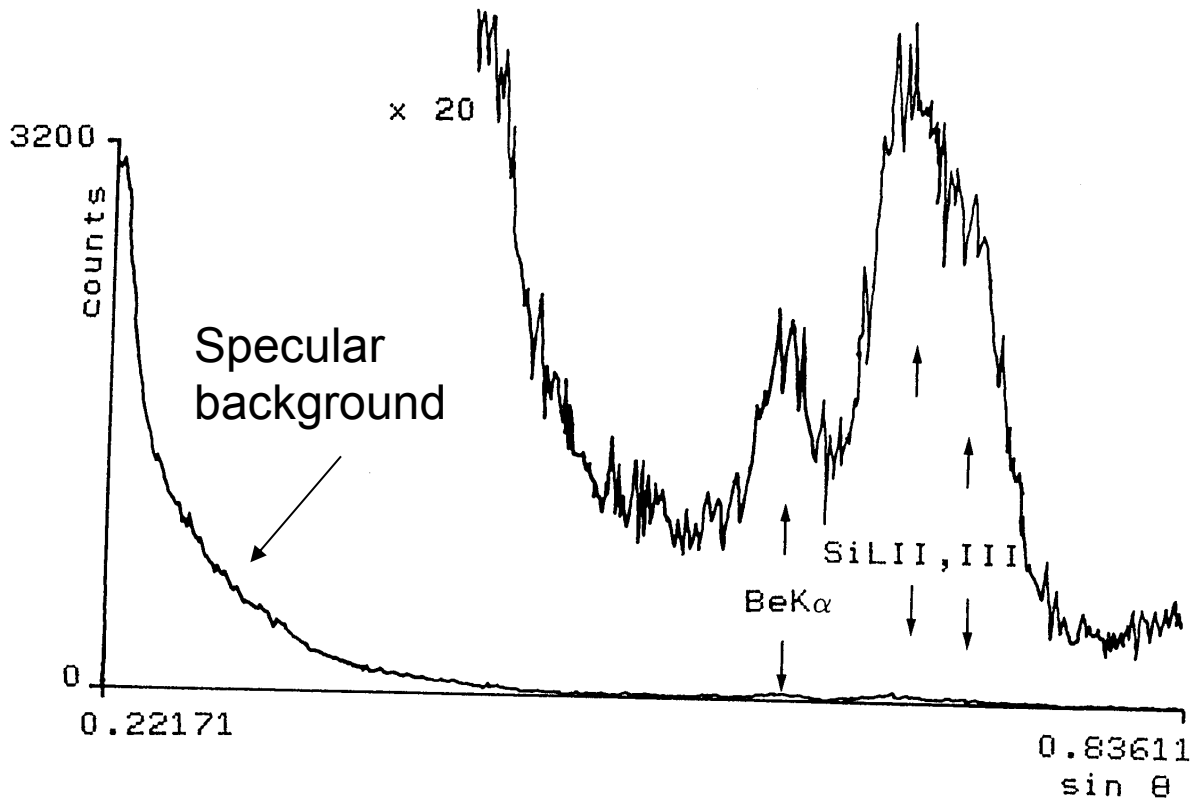


Fig. 5.11. **Bragg reflection**: diffracted rays are in phase when distance $A'B'C'$ differs from ABC by an integral number of wavelengths.

Modélisation du fond continu

Example 1: analysis of beryllium in silicates

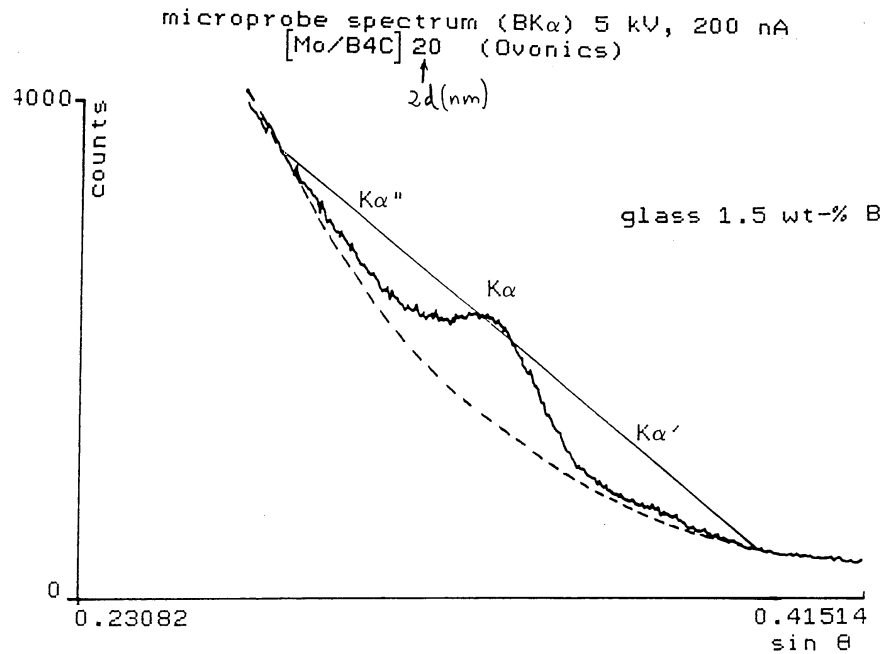
exp. spectrum (microprobe)
for beryl
10 kV, 100 nA,
[Mo/B₄C] 200 (Ovonics)



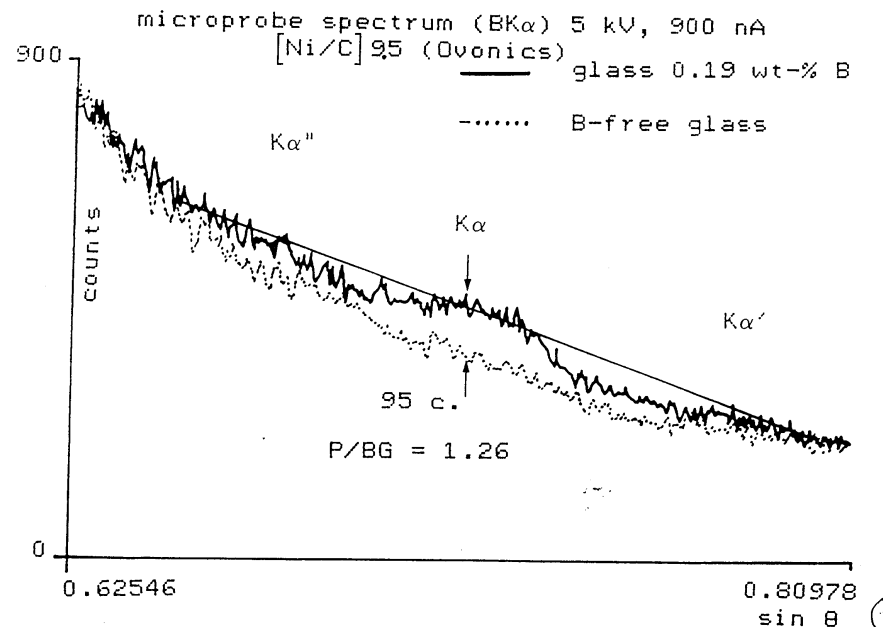
Specular reflection: X rays are totally reflected at the Surface of the LSM giving an intense signal for low Bragg angles. The higher the density of the LSM, the higher the specular reflection

Experimental spectrum recorded from beryl with Mo-B₄C LSM over the full mechanical range of a Cameca WDS. Note the high-level specular background compared with the height of the detected Bragg peaks.

Modélisation du fond continu



Using a Mo/B₄C LSM with 2d=20nm, the B K α peak (composed of a main peak and two satellite peaks K α' and K α'') is recorded over the low- θ range of the spectrometer. The specular background is large and strongly curved.



Using a Ni/C LSM with 2d=9.5nm, 1) lowers the density of the LSM and, 2) shifts the peak towards the high- θ range of the spectrometer where the specular background is reduced. The peak/background ratio for B K α emitted from a 0.19wt-% B glass is the same as that for the B K α peak emitted from the 1.5wt-% B glass with the Mo/B₄C LSM. **-> detectability enhanced for the Ni/C LSM**

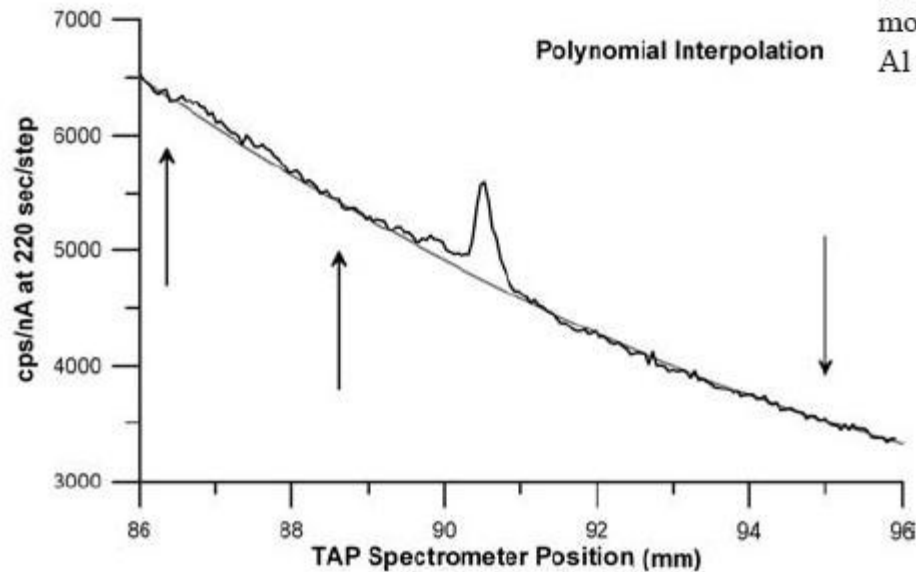
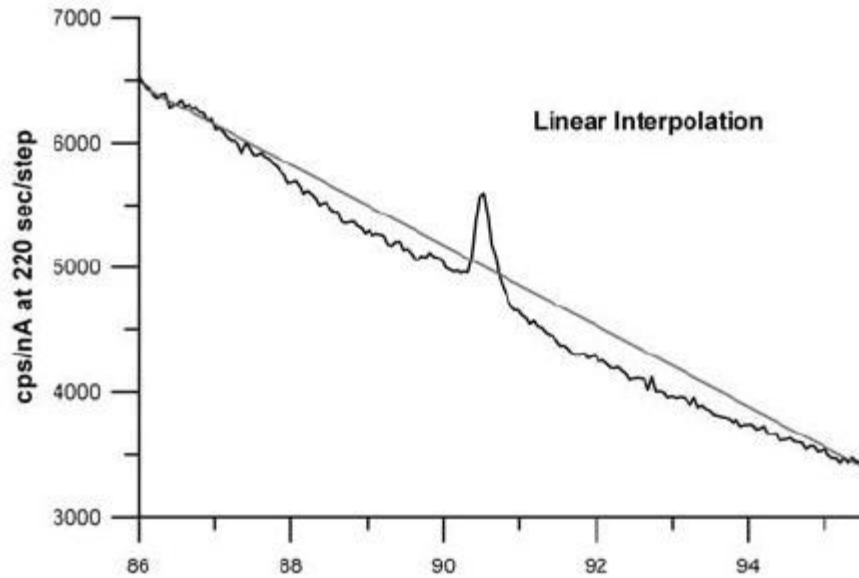


FIGURE 3. Wavelength intensity scan data on hydrothermal quartz in the range of the $AlK\alpha$ peak position (black lines). The gray lines represent different background models: linear (top) and polynomial (bottom). The arrows indicate the selected fit positions for the polynomial fit regression model. The choice of background model significantly affects the apparent Al abundance.

Modélisation du fond continu

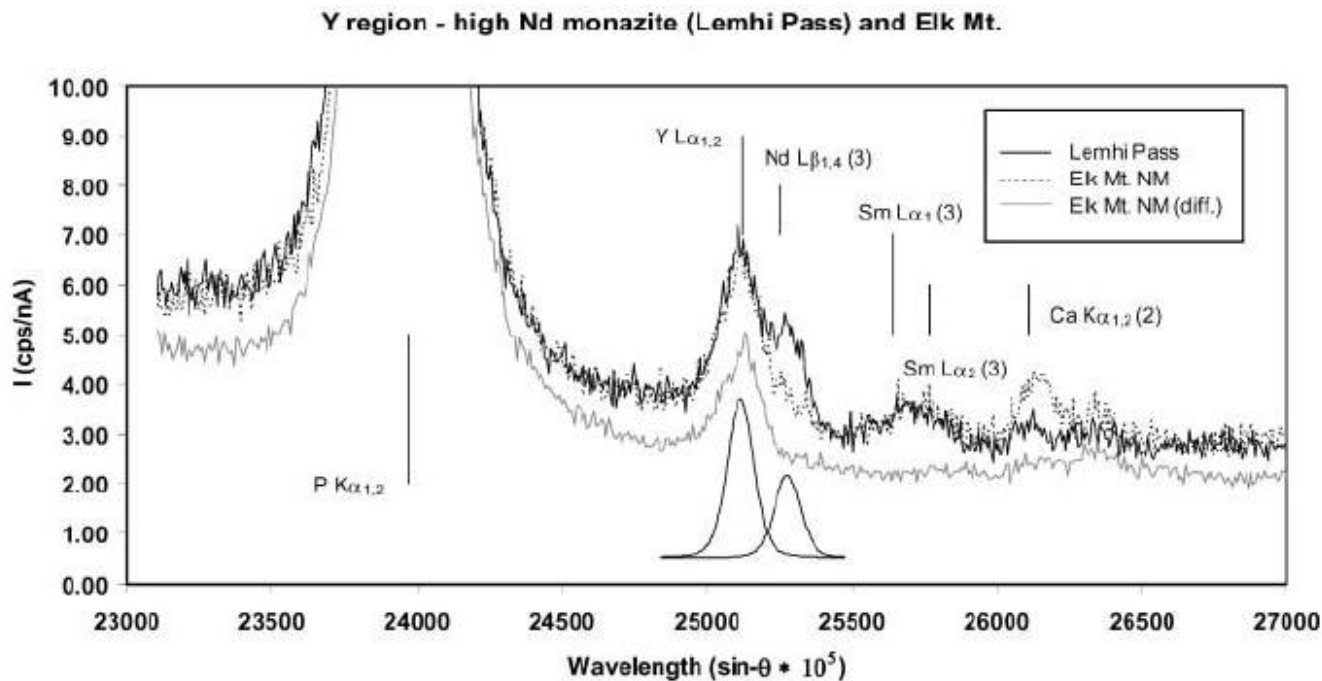


FIGURE 13. Wavelength scans of the $YL\alpha$ region (TAP) from high-Nd monazite from the Lemhi Pass Thorium district, Idaho (29–30 wt% Nd, 0.5 wt% Y), compared to Elk Mt. monazite (9.1 wt% Nd, 0.7 wt% Y). Note the $YL\alpha$ peak shape difference from integral to differential (diff.) PHA modes in the Elk Mt. monazite, illustrating the reduction of the of the $NdL\beta_{1,4}$ (3rd order) line. The deconvoluted peak profiles (background subtracted) for the Lemhi Pass monazite are shown at the bottom of the figure.

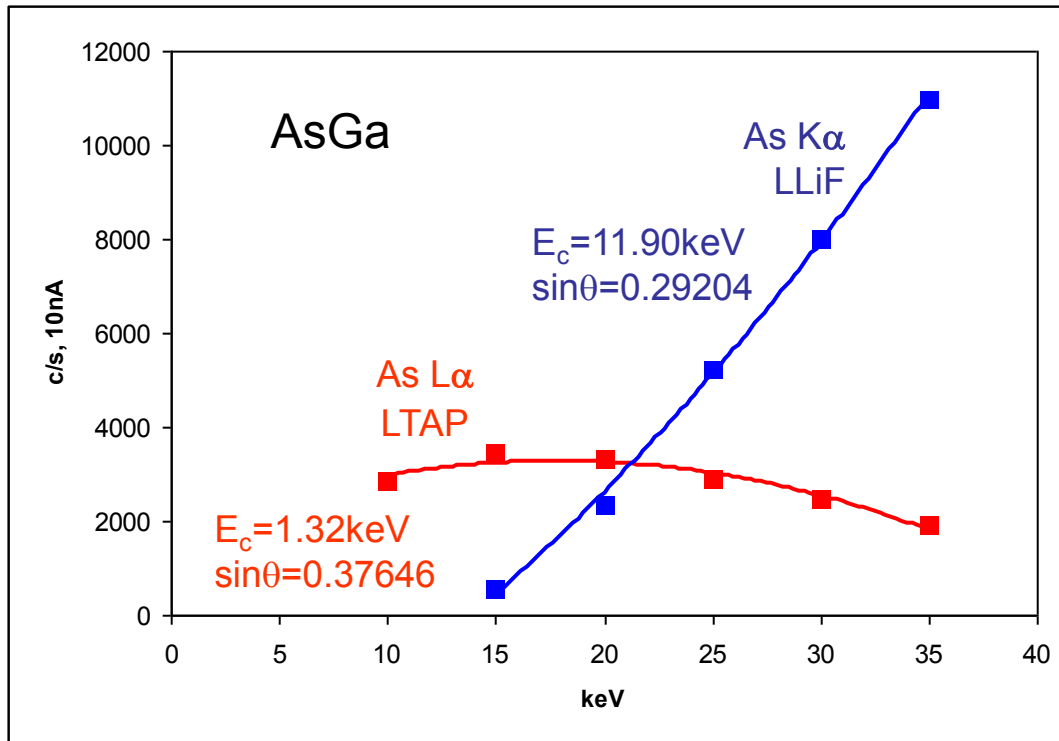
Choix de la raie d'analyse – tension d'accélération

De préférence, choisir toujours (si possible) la raie la plus énergétique et la plus intense...

dans l'ordre : $K\alpha$, $L\alpha$ et $M\alpha$

! Cependant, en cas de forte interférence on peut choisir une raie moins intense ($K\beta$, $L\beta$, $L\eta$, $M\xi$...)

Éléments à choix multiples



Interférences:

As $K\alpha$ (1) – Pb $L\alpha$ (1)
 $\Delta\sin\theta = 0.00022$

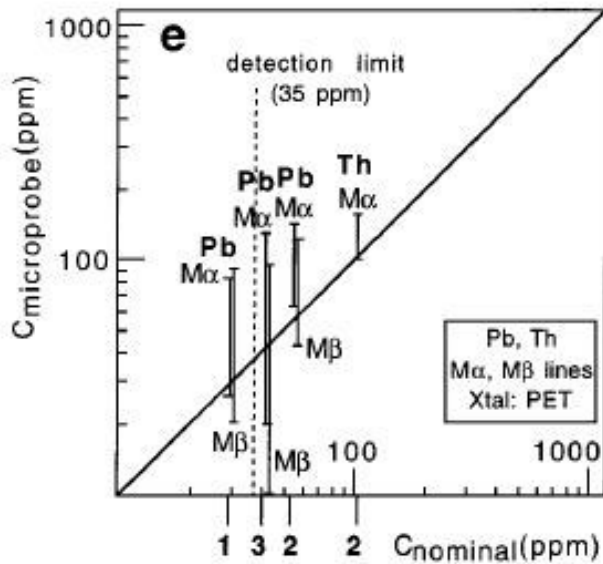
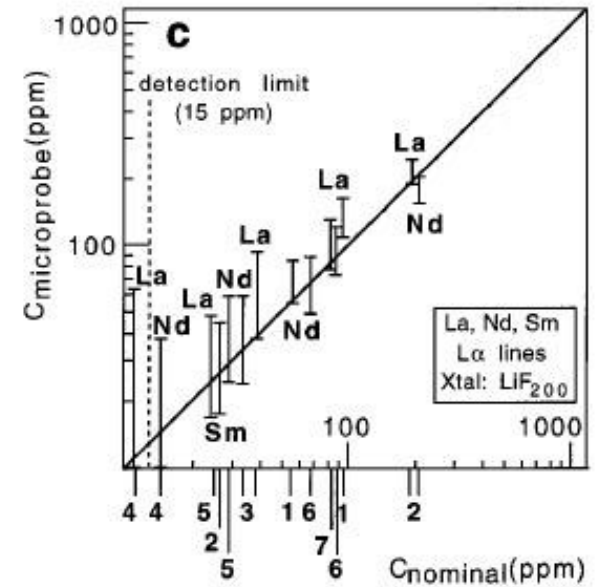
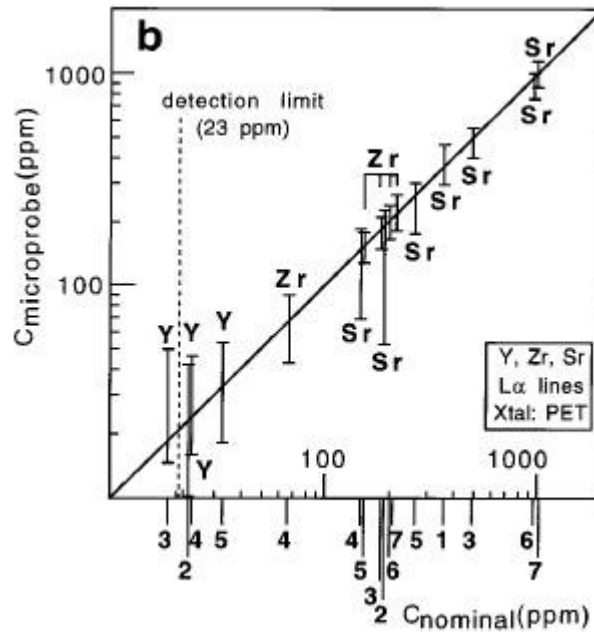
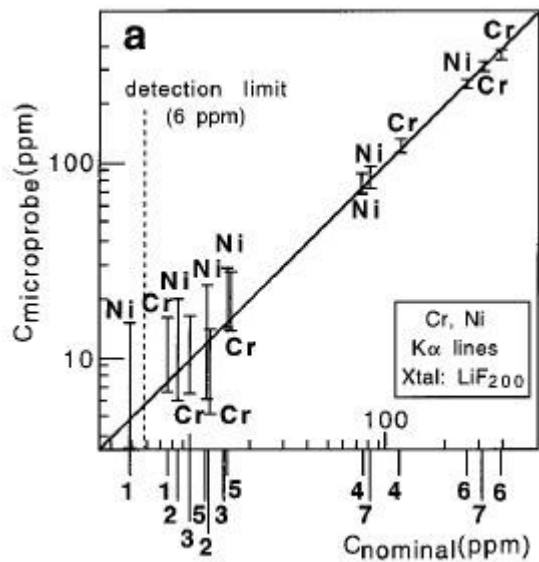
As $L\alpha$ (1) – Fe $K\alpha$ (5)
 $\Delta\sin\theta = -0.00042$

Choix du temps de comptage

Très variable, de quelques centièmes de seconde à plusieurs dizaines de minutes !

Il dépendra :

- de l'élément analysé
- de sa teneur
- de la raie utilisée
- du type de travail (analyse ou cartographie)
- de la précision statistique recherchée...

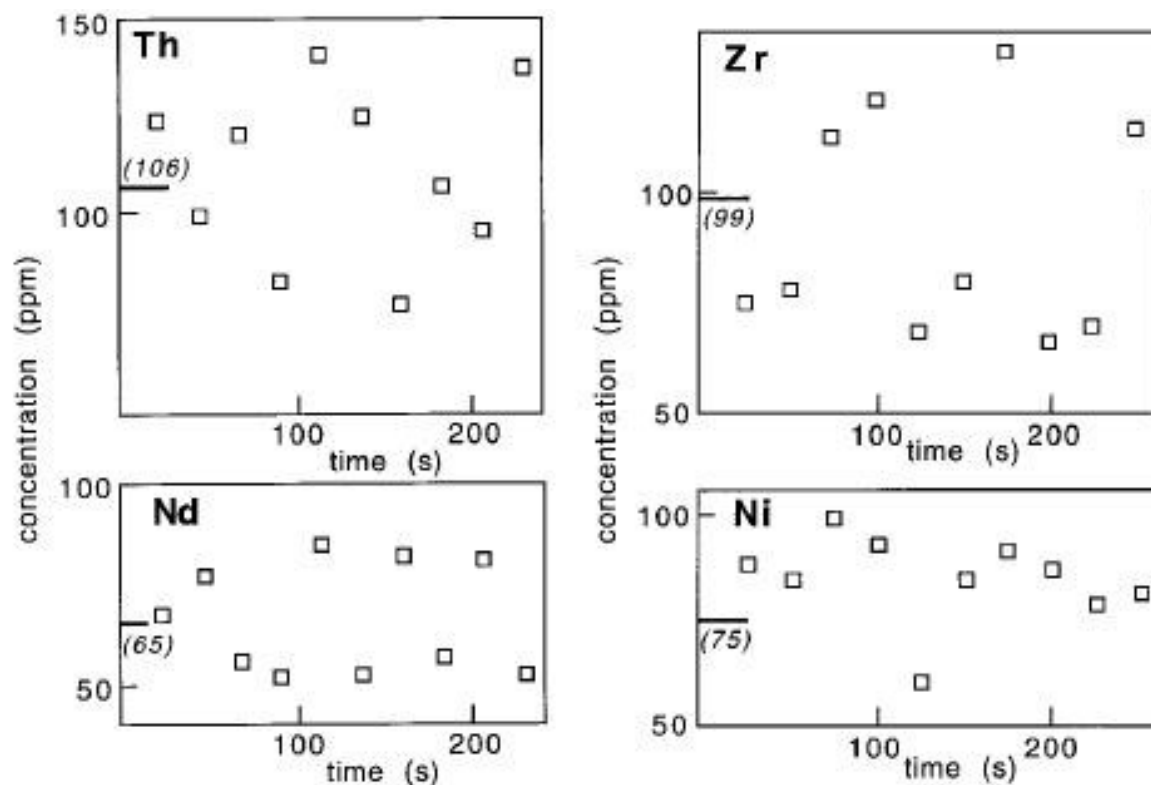


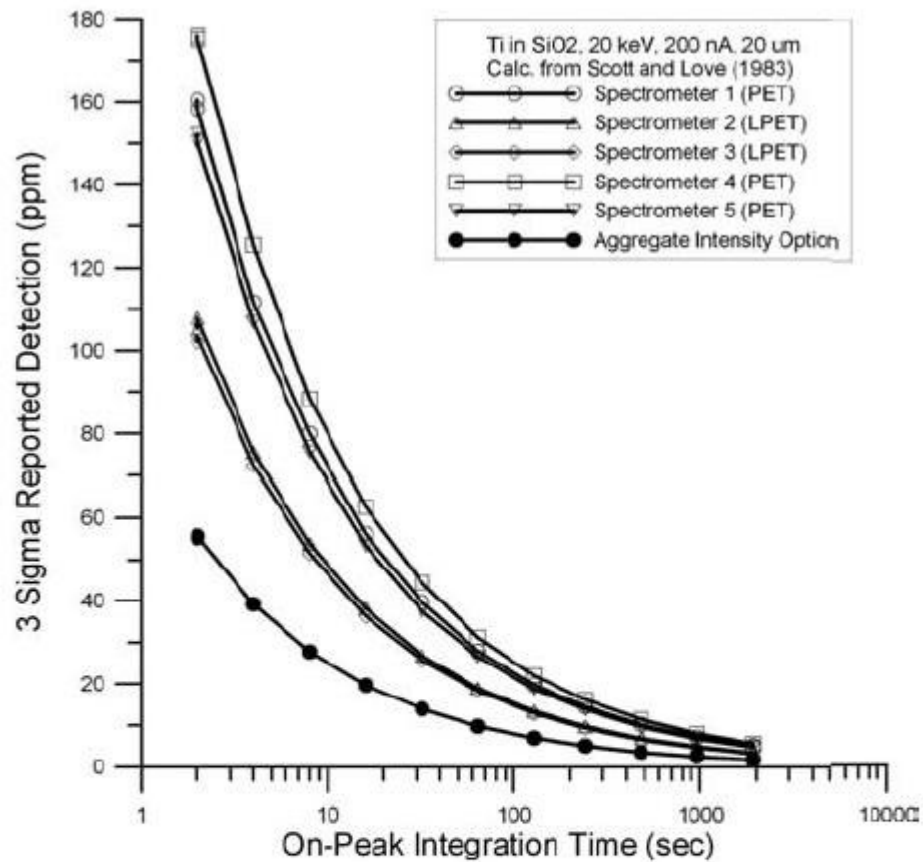
Verres étalons

35kV, 500nA, 10 μ m, t= 1000s (25sitesx40s/site)

Choix de l'intensité du faisceau électronique: dégâts d'irradiation

FIGURE 5. Beam damage tests. Plots were made using data from ten consecutive analyses on a single site. Six runs collected from distinct sites were averaged to improve precision. Error bars were omitted for clarity. The bold bar on the Y axis refers to the nominal value given in parenthesis.



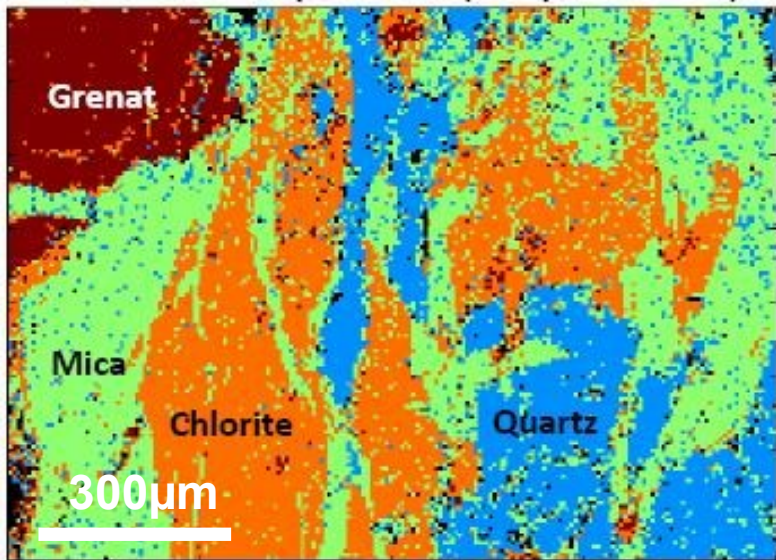


Mesure par couplage de plusieurs spectromètres

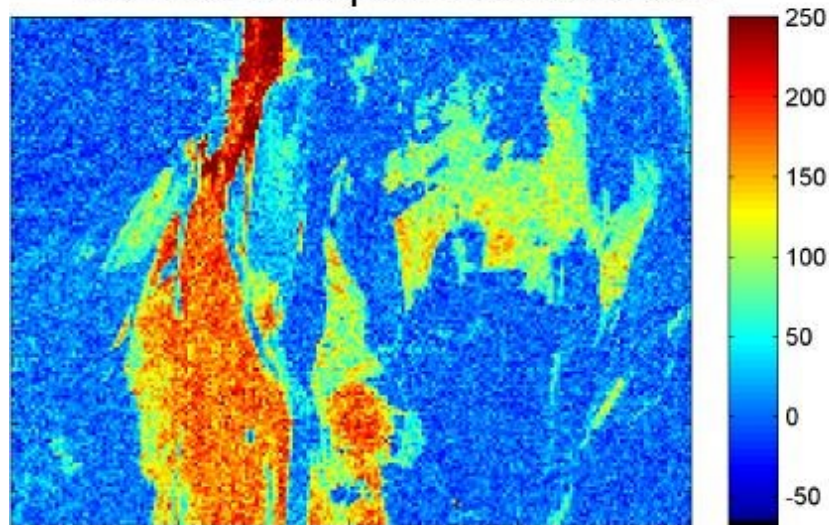
FIGURE 6. Comparison of individual spectrometer 3σ detection limits with the software-enabled “aggregate” intensity option as a function of counting time as measured on a pure SiO₂ “blank” (1.42 ppm Ti by ICP-MS). The aggregate intensity option reflects the combined intensities of all 5 individual spectrometers. Data was acquired on a Cameca SX-100 with 5 spectrometers using PET and LPET crystals. Note that the large area crystals produce the lowest detection limits for an individual spectrometer, but the aggregate intensity option curve consisting of the combined intensities from all 5 spectrometers greatly outperforms any individual spectrometer’s performance.

Ni K α , 20kV, 250nA, 1LiF+2LLiF, 200x150 pixels, 150ms/pixel (2h50mn, P+BG)

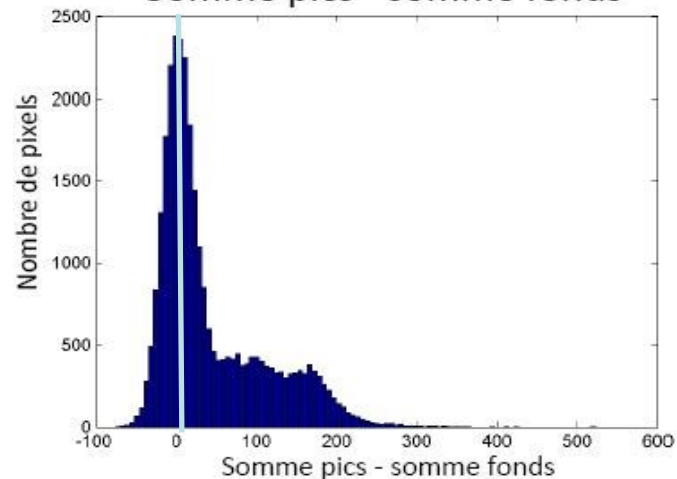
Carte des phases (d'après BSE)



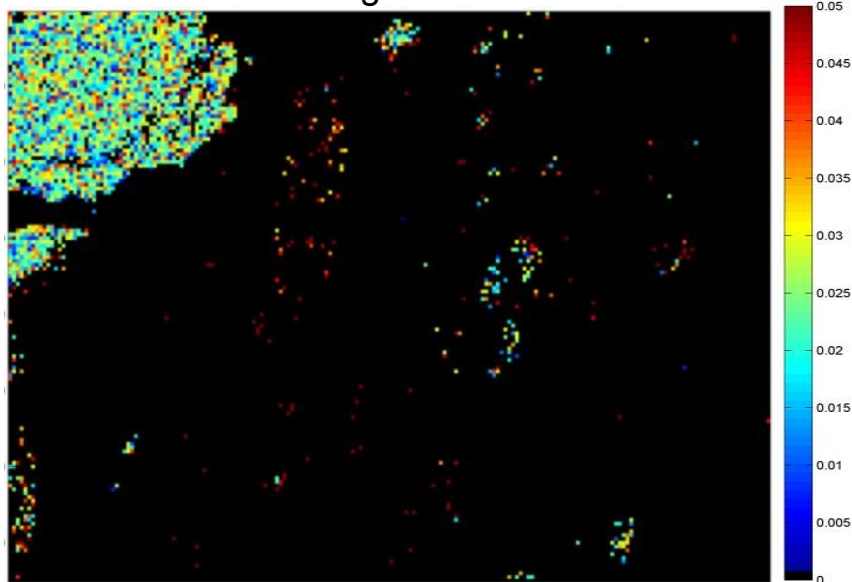
Carte somme pics - somme fonds



Histogramme de fréquence
Somme pics - somme fonds



Pixels grenat



Grenat, 2888pixels (~15mn)

17±6 ppm (2 σ)

(5-10ppm LA-ICPMS)

C_{min} = 4ppm