Metallic Glasses of the Type Fe80B17X3; a SIMS Study

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Abstract

Absolute and relative practical sensitivities for $O_2^+$-bombardement of 14 elements, present as a 3 at% admixture in a $Fe_{80}B_{17}X_3$ metallic glass matrix, were determined by SIMS. The variation of sensitivity data between elements is similar to that found for pure element samples. The 3 % admixture causes a small but statistically significant matrix effect on the matrix elements Fe and B. Comparison with yield data of the same minor impurity elements in other matrices (stainless steel, silicon) shows, that sensitivities in different matrices are within 30 % for most elements, indicating the possibility of transferring relative sensitivity factor data determined on metallic glasses to other Fe-based alloys and thereby obtaining a semi-quantitative analysis.

Zusammenfassung

Absolute und relative praktische Empfindlichkeitsfaktoren wurden für 14 Elemente (als 3 %ige Beimengungen in einer $Fe_{80}B_{17}X_3$ metallischen Glas-Matrix) mit Hilfe der Sekundärionen-Massenspektrometrie (SIMS) unter $O_2^+$-Beschuß bestimmt. Die Variation der Empfindlichkeiten aus der MetGlasmatrix ist ähnlich der aus den Reinelementen bestimmten. Die 3 %ige Beimengung von Elementen verursacht einen merklichen Matrixeffekt auf die Empfindlichkeiten der Matrixelemente Fe und B. Ein Vergleich mit Empfindlichkeitsdaten der gleichen Elemente aus anderen Matrizen zeigt, daß die meisten Elemente innerhalb von $\pm$ 30 % liegt. Dies weist darauf hin, daß die Empfindlichkeitsfaktoren, die für MetGläser bestimmt wurden auch auf andere Fe-Legierungen übertragen werden können und daß damit eine semiquantitative Analyse ($\pm$ 30 % - $\pm$ 50 %) möglich sein müßte.
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1. Introduction

It is wellknown that quantitation of the SIMS method has difficulties, first of all because of the lack of practically usable theoretical models. For this reason, the quantitative evaluation of SIMS spectra yields better analytical results when the method of relative sensitivity factors (RSF) is used /1/-/4/. It was however found that alloying an element to a given matrix or changing the matrix composition can change the matrix and trace element yields (so-called "matrix effect" /5/, /6/). An even more complicated situation may arise when a greater number of components is present in the sample or when concentrations are varying over a wide range; in this case relative sensitivity factors of elements generally are mutually interdependent and empirical quantitation algorithms only yield accurate results when standard sample and unknown sample are similar in constitution and concentration /1/. Furthermore it was shown that instrumental effects can drastically influence the results of quantitative SIMS analysis. Even identical samples, analyzed on instruments of the same type and manufacturer in different laboratories, can produce raw yield data differing by a factor of up to 50 /7/, a factor of 10 remaining even after presumably quantitative correction /8/.

Two requirements therefore seem to be essential for the relative sensitivity factor quantitation algorithm to yield accurate results:

a) a method should be available for tuning a particular SIMS instrument in a way as to yield reproducible raw data when the sample is analyzed at different times and to correct for small deviations from reproducibility (even more interesting would be a method for tuning different instruments to yield reproducibly similar relative intensity data; first results have been obtained /9/ using a procedure similar to that described in section 4).
b) Standard samples should be available for a wide range of elements and concentrations.

Difficulties have however been reported concerning the commonly used standard samples /3/, /4/, /1/, /10/. We consider the metallic glasses to be suitable standards for quantitative SIMS for several reasons:

1) The standard alloys are often inhomogeneous on a micro-scale, owing to the segregation of several elements and to the presence of insoluble phases /1/, /3/, /4/, /10/. The metallic glasses can serve as better standards, because no concentration gradient may occur in the μm scale, and because they are single phase systems.

2) The concentration range of the alloying components is generally limited in crystalline standards because of metallurgic reasons. Metallic glasses can be prepared in a broader concentration range. Even insoluble elements can form an amorphous phase. The number of systems forming an amorphous phase under suitable conditions is relatively broad.

3) The ion yields of elements from crystalline samples depend also on the orientation of the bombarded surface /11/. In the isotropic amorphous systems such effects which may cause errors in the analysis cannot occur.

We have to report here that Newbury /3/ for similar reasons considers the silicon-based ("conventional") glasses as suitable standards. The metallic glasses seem to be better because of the metallic character and broader range of compositions.

Only few SIMS-investigations of metallic glasses have been reported so far. Blum and his co-workers /12/ checked the purity of Fe_xB_{1-x}-type amorphous thin films. Cahn et al. /13/ made use of SIMS to determine the diffusion coefficient of boron in Fe-Ni-B glass. Vasilyev et al. /14/ have published
measurements concerning the difference in ion yield of atomic and cluster ions from the "equilibrium" and from the "non-equilibrium" phase of the iron-boron alloy. Buhl and Preisinger /15/ reported that the SIMS spectrum of amorphous alloys changed during crystallisation. The process has also been followed by X-Ray diffraction method. All the investigations mentioned were focused on one or at most two particular alloys. A comparative SIMS study encompassing a larger variety of metallic glasses has not yet been published.

It was the aim of this work

a) to provide relative sensitivity factor data to be used for quantitative analysis of the Fe - B metallic glasses using well characterized ternary metallic glasses as calibration standards;

b) to check, whether these data can be used for quantitation of other Fe - based alloys;

c) to investigate fundamental aspects of secondary ion emission from binary and ternary metallic glass systems.

2. The Metallic Glass Structure

The majority of the metals and metallic alloys is of poly-crystalline structure in the solid phase, i.e. generally a mixture of single crystals of different composition and orientation. In contrast the structure of the amorphous materials is very close to that of liquids, i.e. without any crystalline order, but with internal friction of the order of magnitude as that of solids (~ 10^{12} Pa s). Chemically the amorphous metallic systems (metallic glasses or amorphous alloys) contain at least two elements: a metal and a metalloid with a composition close to that of the eutectic. Metallic glasses which have found
practical applications are often many-component systems; they show several important properties (viz.: large tensile strength, ferromagnetism, low corrosion rate etc.) and therefore have received increasing attention during the last decade /16/, /17/.

As to the structure of the metallic glasses it is characteristic that there exists a certain degree of short distance order between nearest neighbor atoms but no long distance order exceeding the nm range. The most important properties are:

- macroscopic isotropy ?
- spatial compositional homogeneity (i.e. random distribution of the constituent atoms
- the metallic - type bonding (in contrast to glasses in the conventional sense)
- the experimentally determined coordination number of the atoms generally between 11 and 13; which represents a packing density close to that found in the densest crystalline metallic lattices.

The best generally applicable model for the metallic glass structure is the "dense random packing of hard spheres" (DRPHS), which was introduced by Bernal in 1964 /18/. According to this model, 5 geometric patterns exist which satisfy the demand of random close packing of atoms. The metal atoms occupy the vertices of polyhedral configurations and being generally small, the metalloid atoms can be fitted into their "holes". The characteristic radius of the short distance order (as determined by X-ray diffraction) can be regarded as the diameter of these polyhedral patterns. On a larger scale (exceeding 1,5 nm) random structure and elemental composition is found. At present, more than 30 alloy systems are known which can form a metallic glass phase under proper conditions. There are several methods for producing the amorphous state (electro-
chemical, electroless deposition, vacuum evaporation etc.) from among which the most universally applicable is extremely rapid cooling of the molten alloy ("superquench"). The cooling rate has to be at least $10^5$ K/s.

3. Experimental

Experiments were performed on the Seibersdorf quadrupole scanning ion microprobe described elsewhere /19/, /20/. The pressure in the target chamber was in the $10^{-3}$ torr range during the measurements with the ion gun in operation. A mass filtered primary $O_2^+$-beam of 10 keV energy was produced in a differentially pumped duoplasmatron ion source, focused to a diameter of about 50 μ at the target and rastered with normal incidence across an area of 200 x 200 μ for sputter cleaning of the sample; after reaching steady-state conditions (characterized by a constant matrix ion signal) the rastered area was reduced to a size of 100 x 100 μ for the actual measurement. Usually, a surface layer of the order of 100 nm thickness was sputtered off during the precleaning procedure. The primary ion current was in the range of 20 nA and was measured by a Farady cup arrangement. Secondary ions were analyzed by a commercially available energy analyzer/mass filter arrangement (RIBER SQ 156) and detected by an open multiplier operated in the pulse counting mode. Secondary ion yield measurements were performed on two analytical areas (100 x 100 μ) of each sample. Three limited range mass spectra of singly charged positive atomic ions were recorded in each analytical area, covering the isotopic range of B, Fe and the X-element respectively; the isotope peak heights were automatically extracted from the mass scans and appropriately averaged for each set of spectra. Instrument control and data acquisition was fully computerized using a stand-alone PDP 11/34 computer and CAMAC I/O system /20/.
The elemental compositions of the two series of metallic glass alloys studied were:

a) Fe - B with 11.7, 16.6 and 21.6 atomic per cent boron content;

b) Fe\textsubscript{80-B\textsubscript{17}}X\textsubscript{3}, where X stands for a transition metal of the 3 d, 4 d and 5 d periods (V, Cr, Mn, Co, Ni; Nb, Mo, Ru, Rh, Pd; Ta, W, Os, Ir). The concentration of the element X was generally 3.0 at % with a precision of better than \pm 0.2 at % with the exception of V (3.8 at %) and Mn (1.5 at %).

The samples have been prepared in the Central Research Institute of Physics of the Hungarian Academy of Sciences using the method of rapid quenching from molten metal alloys of high purity. The cooling rate was about \(10^6\) K/s. The composition of the samples was checked by atomic absorption analysis /21/ and the homogeneity by electron microprobe measurements. Our SIMS measurements proved that the concentration of impurities is generally below the detection limit (10-50 ppm). The amorphous state of the samples has been verified by X-ray diffraction methods.

The samples were in the shape of long strips of approximately 1 mm width and 25-35 \(\mu\) thickness. Short pieces of 1 cm length were cut from these strips and spot - welded to a supporting 1 cm x 1 cm Ta foil with the exception of the Fe-B-Ta sample which was mounted on a Mo-foil.

4. Data Evaluation

The detected positive secondary ion current \(I^+\) (X) (summed over all isotopes) of atomic ions of an element X which is

* The authors wish to express their thanks to Dr. A. Lovas for supplying the samples.
present in a relative fractional atomic concentration \( c \) (x) in a sample may be calculated according to the "fundamental SIMS formula" /4/:

\[
I^{+\prime}(X) = I_p \cdot y_{tot} \cdot c(X) \cdot \alpha^+(X) \cdot f(X)
\]  

(1)

where \( I_p \) is the primary ion current, \( y_{tot} \) the total sputter ion yield of the sample, \( \alpha^+(X) \) the degree of positive ionization of atomic particles X and \( f(X) \) the "total instrumental transmission factor" of the SIMS instrument, generally depending on atomic and mass number of element X; \( f(X) \) includes all "discrimination effects" due to optical instrument transmission and detector efficiency. Since for a multielement system \( y_{tot} \) and \( \alpha^+(X) \) cannot be accurately calculated from first principles (matrix effect) and \( f(X) \) critically depends on instrument adjustment (particularly for quadrupole mass analyzers), these variables are combined into an empirical factor \( y^{+\prime}(X) \), the "apparent secondary ion yield" of element X:

\[
y^{+\prime}(X) = I^{+\prime}(X)/I_p = y_{tot} \cdot c(X) \cdot \alpha^+(X) \cdot f(X)
\]  

(2)

The apparent secondary ion yield (=number of detected secondary ions/number of primary ions, measured in units of cps/nA) differs from the "secondary ion yield" \( y^{+}(X) \) of element X (=number of emitted secondary ions X/number of primary ions also measured in cps/nA) only in the instrumental transmission factor \( f(X) \). In order to refer yields and apparent yields of element X always to the same number of atoms X present in the sample, it has become customary to divide \( y^{+\prime}(X) \) by the concentration \( c(X) \); this new parameter is called the "practical sensitivity" \( S^p_p \) of a particular SIMS instrument for element X /22/:

\[
S^p_p(X) = I^{+\prime}(X)/I_p \cdot c(X) = \frac{y^{+\prime}(X)}{c(X)}
\]  

(2a)
The ratio of practical sensitivities for elements X and y is called the "relative practical sensitivity" (or "relative sensitivity factor" RSF (X)) of element X, referenced to element y /1/:  

\[
\text{RSF} (X) = \frac{S_p (X)}{S_p (y)} = \frac{I^+ (X) / c (X)}{I^+ (y) / c (y)} = \frac{\alpha^+ (X)}{\alpha^+ (y)} \cdot \frac{f (X)}{f (y)}
\]  

(3)

For a given element X, the practical sensitivity generally depends strongly on the instrument type (the instrument acceptance entering into the transmission factor f(X)). The relative sensitivity factor RSF (X) principally may become independent of the instrument type since, by proper choice of operating conditions the (mass dependent) transmission function f of one instrument can be made approximately proportional to that of another instrument (at least for a limited mass range).

In the context of this work, absolute and relative practical sensitivities of a great number of elements, differing in mass number by factor of almost 20 have to be compared. The data were taken during a measuring period extending over more than two weeks so that special care had to be taken to avoid the problems connected with instrument drift and reproducibility of measurements. Furthermore, it was the goal of these measurements to provide relative sensitivity factor data for quantitation of unknown samples from the Fe-B-X system which should remain valid and reproducible at any measurement period following the first measurements. It was observed during the measurements that sensitivity values critically depend on the adjustment of instrument parameters. A method has therefore to be developed which allows to verify that the instrument is adjusted the same way as during the original measurement of the appropriate sensitivity factors and which allows to compensate for small deviations from the original "standard adjustment". In this work we have used a phenomenologic standardization
procedure which we have called the "PCS method":

1) A "primary calibration standard (PCS)" is chosen; this should be a well characterized homogeneous sample containing elements with mass numbers spread out over as large a mass range as possible. The metallic glass sample Fe$_{80}$B$_{17}$W$_3$ from the Fe-B-X system described in section 2 fulfills these requirements.

2) "Standard operating conditions (SOC)" are defined. These include primary beam parameters (element, energy, current, current density, angle of incidence, etc.), and target related parameters (sample preparation, presputtering, residual gas pressure, oxygen bleeding-in pressure, etc.) as well as mass analyzer parameters (energy window, extraction optics, pre-analyzer focusing elements, rod voltages, post-analyzer focusing elements, detector voltages, etc.). In the secondary ion mass analyzer used for these measurements the latter group of adjustments involves the manual setting of 17 voltage controls. The parameters of the SOC are given in tab.1.

It is well known that mass transmission and mass resolution of a quadrupole, amongst others, depend sensitively on the d.c./a.c. voltage ratio and on the d.c. bias applied to the rods. Both, constant peak width and constant mass resolution scans can be principally obtained by proper choice of these voltages. In the first operating mode, transmission in an ideal quadrupole is proportional to 1/M (M...mass number), in the second mode it is independent of mass. An operating mode with constant mass transmission would be preferable for the analysis of the Fe-B-X-systems, because the elemental constituents almost cover the full mass range of the periodic systems, and because of the possibility of using theoretical quantitation algorithms for the determination of the concentrations of unspecified elements; these algorithms only allow the calculation of elemental
concentrations from ion currents \( I^+(X) \) or ion current ratios \( I^+(X)/I^+(Y) \) emitted directly from the target. If however the ratios of the detected currents, \( I^+(X)/I^+(Y) \), deviate from those of the emitted currents (owing e.g. to an unknown mass discrimination of the mass analyser system), quantitation algorithms, applied to the detected current ratios obviously will yield wrong results. A constant transmission can however be achieved for a limited mass range only /23/ and only at the cost of nonoptimal transmission at low masses /22/. Nevertheless, the SOC of tab. 1 are chosen to approximate mass-independent transmission (see section 6). Abandoning this condition, the transmission in an individual narrow mass range (depending on instrument adjustments) may be increased by more than one order of magnitude.

3) "Original Apparent Yields \( OAY(S) \)" and "original calibration ratios \( OCR(S) \)" are determined under SOC for all elements \( S \) in the PCS (in our case of B, Fe and W):

\[
\begin{align*}
OAY(S) &= \frac{I^+(S)}{I^+_P(S)} \\
OCR(S) &= \frac{I^+(S)}{I^+(Fe)}
\end{align*}
\quad S = B, Fe, W \quad (4)
\]

These (original) apparent yields and yield ratios are determined once with great accuracy and will be a reference for any future quantitative measurement on the system Fe-B-W which are done with the particular SIMS instrument on which the \( OAY(S) \) and the \( OCR(S) \) have been determined. Numerical values of the \( OAY(S) \) and \( OCR(S) \) for our PCS are given in table 2.

Now, if at any later time quantitative measurements on the Fe-B-W system are to be compared to another set of measurements, the
analyzer has to be retuned in a way that data taken on the PCS can always be reproduced as accurately as possible. For this purpose:

4) the standard operating conditions (SOC), including the mass analyzer settings are again adjusted as closely as possible.

5) the PCS is reanalyzed and "actual apparent yields AAY(S)" and "actual calibration ratios ACR(S)" are determined which now are characteristic for the actual set of measurements only:

\[
\begin{align*}
AAY(S) &= \frac{I^+(S)}{I^+(Fe)} \\
ACR(S) &= \frac{I^+(S)}{I^+(Fe)} \\
S &= B, Fe, W
\end{align*}
\]

In this and all further equations the bars mean averages over the respective variables. In the first equation individual current readings from each scan are averaged for each analytical area and a weight average is formed from the averages of the analytical areas. In the second equation, the same averaging procedure is performed for the ion current ratios from each individual scan. Due to unavoidable inaccuracies in adjustments and due to instrument drift with time, the original values will only be reproduced approximately:

\[
\begin{align*}
AAY(S) &\approx OAY(S) \\
ACR(S) &\approx OCR(S)
\end{align*}
\]

Characteristically, the OAY and OCR are reproduced within \(+9\%\) after readjusting for SOC, which means that the "yield correction factors" (YCF), as defined in (6) below typically take on values of 1.00 \(\pm 0.09\). The statistical precisions of
a determination of an AAY is typically 7% and of an ACR typically 5%. Within the same day, the drift of the measured AAY and ACR for the "calibration elements" B, Fe, W is of the order of 2 - 4%, i.e. smaller than the statistical precision and the uncertainty of the YCF. The instrument drift within one day has therefore not been considered in the data evaluation procedures described below.

6) If necessary, instrument adjustments can be slightly changed to give a better agreement between ACR(X) and OCR(X). Still the actual yields will generally not be exactly reproduced. Therefore, "yield correction factors, YCF(S)" are defined:

\[ YCF(S) = \frac{AAY(S)}{OAY(S)} \quad S = B, Fe, W \]  

(6)

these factors generally will deviate slightly from the value 1.

7) These deviations may be caused by several effects:
a) inaccurate reproduction of external sample related parameters;
b) inaccurate reproduction of mass analyzer voltage settings or aging and drift of quadrupole power supply components.

In the first case shifts of the energy spectrum of secondary ions, e.g. due to different oxidation states of the surface, may influence the apparent yield of an element when the energy preselector has a very narrow bandpass. In the second case it may be assumed that small misadjustments, aging and drift are causing a smooth, although not necessarily a monotonous, change of the transmission function of the mass analyzer, i.e. the yield correction factor YCF(X) of an element X will be a function of its mean mass number \( \bar{M} \) (weighted according to the isotope abundances) only. Consequently, the yield correction factor of any element X, contained in
an unknown sample may be obtained by interpolating between the YCF \( \int \bar{M}(S) \, d\gamma \), \( S = B, Fe, W \):

\[
YCF(X) = YCF \left( \int \bar{M}(X) \, d\gamma = YCF(\bar{M}) \right)
\]  

(7)

In our particular case of the B-Fe-W - standard, \( \bar{M}(B) = 10.81 \), \( \bar{M}(Fe) = 55.85 \), \( \bar{M}(W) = 183.85 \) (see fig. 1)

In our work, we have used a second order polynomial fit

\[
YCF(\bar{M}) = A_0 + A_1(\bar{M} - M_C) + A_2(\bar{M} - M_C)^2
\]  

(8)

which passes exactly through the points for B, Fe, W; \( M_C \) has been chosen to be the mean atomic mass number of Fe, \( M_C = 55.85 \); this choice avoids a systematic bias of the interpolation error towards one side of the mass range (see equation (12) below). The parameters \( A_0, A_1, A_2 \) of the least square fit (8) can be determined as

\[
A_0 = \frac{1}{\Delta} \left[ YCF(B) \cdot D_1 - YCF(Fe) \cdot D_2 + YCF(W) \cdot D_3 \right]^{-1}
\]

(9)

\[
A_1 = \frac{1}{\Delta} \left[ YCF(B) \cdot D_4 + YCF(Fe) \cdot D_5 - YCF(W) \cdot D_6 \right]^{-1}
\]

(9)

\[
A_2 = \frac{1}{\Delta} \left[ YCF(B) \cdot D_7 - YCF(Fe) \cdot D_8 + YCF(W) \cdot D_9 \right]^{-1}
\]

(9)

where the determinant \( \Delta \) is given as

\[
\Delta = \begin{vmatrix}
1 & \bar{M}_1 - M_C & (\bar{M}_1 - M_C)^2 \\
1 & \bar{M}_2 - M_C & (\bar{M}_2 - M_C)^2 \\
1 & \bar{M}_3 - M_C & (\bar{M}_3 - M_C)^2
\end{vmatrix}
\]  

(10)
and the \( D_1 \ldots D_9 \) are subdeterminants of (10) (see tab. 6). For our special choice of \( \bar{M}_2 = M_c \) and \( \bar{M}_1 = 10,81, \bar{M}_2 = 55,85, \bar{M}_3 = 183,85 \), we obtain the following numerical values for the coefficients in (9):

\[
\begin{align*}
\Delta &= 9,97596 \cdot 10^5 \\
D_1 &= 0 \\
D_2 &= -9,97596 \cdot 10^5 \\
D_3 &= 0 \\
D_4 &= 1,6384 \cdot 10^4 \\
D_5 &= 1,43554 \cdot 10^4 \\
D_6 &= -2,0286 \cdot 10^3 \\
D_7 &= 128 \\
D_8 &= 173,04 \\
D_9 &= 45,04
\end{align*}
\]

(11)

The standard deviation, \( \sigma_{YCF}(\bar{M}) \), of the interpolated yield correction factors corresponding to an arbitrary mass number \( \bar{M} \) can be derived from the standard deviations \( \sigma_{YCF}(X) \) of the yield correction factors of the "calibration elements", \( X=B, Fe, W \) as:

\[
\sigma_{YCF}(\bar{M})^2 = \sigma_{YCF}(0)^2 + (\bar{M} - M_c)^2 \sigma_{YCF}(1)^2 + (\bar{M} - M_c)^4 \sigma_{YCF}(2)^2 \tag{12}
\]

where

\[
\begin{align*}
\sigma_{YCF}(0)^2 &= \left( -D_1 \right)^2 \sigma_{YCF}(B)^2 + D_2^2 \sigma_{YCF}(Fe)^2 + D_3^2 \sigma_{YCF}(W)^2 - 7/\Delta^2 \\
\sigma_{YCF}(1)^2 &= \left( -D_4 \right)^2 \sigma_{YCF}(B)^2 + D_5^2 \sigma_{YCF}(Fe)^2 + D_6^2 \sigma_{YCF}(W)^2 - 7/\Delta^2 \\
\sigma_{YCF}(2)^2 &= \left( -D_7 \right)^2 \sigma_{YCF}(B)^2 + D_8^2 \sigma_{YCF}(Fe)^2 + D_9^2 \sigma_{YCF}(W)^2 - 7/\Delta^2
\end{align*}
\]

Again, for the particular choice of calibration elements and mass scale origin, the determinants \( \Delta \) and \( D_1 \) take on the
values given in (11), and (12) can be written with (12a) as:

\[
\begin{align*}
\sigma^2 (A_0) &= \sigma^2_{YCF}(Fe) \\
\sigma^2 (A_1) &= 2.6973 \times 10^{-4} \cdot \sigma^2_{YCF}(B) + 2.07072 \times 10^{-4} \cdot \sigma^2_{YCF}(Fe) \\
&\quad + 4.13508 \times 10^{-6} \cdot \sigma^2_{YCF}(W) \\
\sigma^2 (A_2) &= 1.6431 \times 10^{-8} \cdot \sigma^2_{YCF}(B) + 3.00873 \times 10^{-8} \cdot \sigma^2_{YCF}(Fe) \\
&\quad + 2.03839 \times 10^{-9} \cdot \sigma^2_{YCF}(W)
\end{align*}
\]

The standard deviations of the YCF's of the calibration elements, \( \sigma_{YCF}(S) \), can be calculated from the standard deviations of the \( \text{AAY}(S) \) and of the \( \text{OAY}(S) \), measured on the day of re-analysis and of the original analysis of the PCS respectively (see equ. (6)):

\[
\sigma^2_{YCF}(S) = \frac{\sigma^2_{YCF}(S)}{\sigma^2_{AAY}(S)/\sigma^2_{OAY}(S)} = \left( \frac{\sigma^2_{AAY}(S)}{\sigma^2_{AAY}(S)} \right) - \left( \frac{\sigma^2_{OAY}(S)}{\sigma^2_{OAY}(S)} \right) - \left( \frac{\sigma^2_{AAY}(S)}{\sigma^2_{AAY}(S)} \right) - \left( \frac{\sigma^2_{OAY}(S)}{\sigma^2_{OAY}(S)} \right) - \left( \frac{\sigma^2_{AAY}(S)}{\sigma^2_{AAY}(S)} \right) - \left( \frac{\sigma^2_{OAY}(S)}{\sigma^2_{OAY}(S)} \right)
\]

where the \( \text{AAY}(S) \) themselves are appropriately averaged values from a series of individual measurements on different analytical areas.

When now, on a particular day an "unknown sample" is analyzed in order to determine the yields \( Y(X) \) of elements \( X \) not contained in the PCS, the following steps have to be taken:

8) determine the actual yields \( \text{AYU}(\bar{M}) \) of elements \( X(\bar{M}) \) in the unknown sample

\[
\text{AYU}(X) = \frac{I^*(X)}{I_p}
\]
where \( i^+(X) \) should be the sum over all elemental isotopes;

9) interpolate the yield correction factors \( YCF(\bar{M}) \) of the "unknown" elements \( X \) between the yield correction factors of the "calibration elements" \( B, \) \( Fe, \) \( W, \) valid for that particular day and finally calculate the "corrected yield" \( CYU(X) \) of the unknown element

\[
CYU(X) = AYU(X)/YCF(\bar{M})
\]

(15)

The \( CYU(X) \) represents the yield of the unknown element if it would have been measured at the same day as the \( OAY(S) \) and therefore form a basis for comparison of yields of different elements contained in the \( B/Fe \) matrix which have been measured during different measuring periods. The standard deviation of the corrected yield \( CYU(X) \) can be calculated from equs. (13) and (15):

\[
\sigma^2_{CYU(X)} = CYU^2(X)/AYU^2(X) + \sigma^2_{YCF(\bar{M})}/YCF(\bar{M})^2
\]

(16)

The practical sensitivities \( S_p(X) \) of elements \( X \) (shown e.g. in fig. 2) are obtained from the corrected yields \( CYU(X) \):

\[
S_p(X) = CYU(X)/c(X)
\]

(17)

where \( c(X) \) is the fractional atomic concentration of the
"unknown" element X. The error bars shown in fig. 1 and tab. 3 represent the standard deviation of \( S_p \), \( \sigma_p(X) \):

\[
\sigma_p(X) = S_p(X) \cdot \left| \frac{\sigma_{CYU}(X)}{CYU(X)} \right|
\]  

(18)

For the determination of the relative practical sensitivities of elements X (= relative sensitivity factors, RSF) with respect to the matrix element Fe it is preferable to form ion current ratios X/Fe immediately in each spectrum and average these over all spectra and analytical areas rather than form the ratios of the elemental practical sensitivities, determined according to (15) and (17). A considerably smaller experimental error can be expected from this measure. A similar data evaluation procedure as used in the determination of the CYU(X) is suggested:

Steps (1) - (3), comprising the original measurements on the primary calibration standards (PCS), are identical to the procedure used in the determination of the CYU(X); also, the same standard operating conditions (tables 1 and 2) are used.

5a) Immediately before the measurement of an unknown element, the PCS is reanalyzed under the same SOC and the "actual calibration ratios" ACR(S) of the calibration elements B, Fe, W are determined from the averages of individual current ratios (5) from different scans and analytical areas:

\[
ACR(S) = \frac{I^+(S)}{I^+(Fe)} \quad S = B, Fe, W
\]  

(19)

6a) "Ratio correction factors" RCF(S) are determined for the calibration elements
RCF(S) = ACR(S)/OCR(S) \quad S = B, W \quad (20)

and

RCF(Fe) = 1

7a) Assuming again, that the deviations of the RCF(X) from the value 1 are due only to a slight change of the mass dependence of the quadrupole transmission, the ratio correction factor of any element X can be considered a function of its mean elemental mass \( \bar{M} \) only and can be interpolated between the RCFs for the calibration elements B, Fe, W:

RCF(X) = RCF(\( \bar{M}(X) \)) for any element X \quad (21)

Again, a third order polynomial fit is used with \( M_c = \bar{M}(Fe) = 55.85 \).

RCF(\( \bar{M} \)) = \( A_0 + A_1(\bar{M} - M_c) + A_2(\bar{M} - M_c)^2 \) \quad (22)

The \( A_i \) are determined by an equation similar to (9). Considering that RCF(Fe) = 1, we obtain in the present case:

\[
\begin{align*}
A_0 &= \sum RCF(B) \cdot D_1 - D_2 + RCF(W) \cdot D_3 \div \Delta \\
A_1 &= \sum RCF(B) \cdot D_4 + D_5 - RCF(W) \cdot D_6 \div \Delta \\
A_2 &= \sum RCF(B) \cdot D_7 - D_8 + RCF(W) \cdot D_9 \div \Delta
\end{align*}
\]

(23)

where the values of the \( D_i \) and \( \Delta \) are the same as given
in (7). Since the standard deviation of \( RCF(Fe) \), \( \sigma_{RCF}(Fe) = 0 \), and since also \( D_1 = D_3 = 0 \), the expressions (12) and (12a) for the standard deviations \( \sigma^2_{RCF}(\bar{M}) \) for an arbitrary element with mean mass number \( \bar{M} \) simplify to

\[
\sigma^2_{RCF}(\bar{M}) = (\bar{M} - \bar{M}_c)^2 \cdot \sigma^2(A_1) + (\bar{M} - \bar{M}_c)^4 \cdot \sigma^2(A_2)
\]  

(24)

and

\[
\sigma^2(A_1) = \left\{ -D^2_4 \cdot \sigma^2_{RCF}(B) + D^2_6 \cdot \sigma^2_{RCF}(W) \right\} \frac{1}{\Delta^2} \\
\sigma^2(A_2) = \left\{ -D^2_7 \cdot \sigma^2_{RCF}(B) + D^2_9 \cdot \sigma^2_{RCF}(W) \right\} \frac{1}{\Delta^2}
\]

(24a)

where the \( \sigma^2_{RCF}(S) \) can be derived from the definition of the ratio correction factors (20):

\[
\sigma^2_{RCF}(S) = \frac{RCF(S)^2 \left\{ \sigma^2_{ACR}(S)/ACR(S) \right\}^2 + \left( \sigma^2_{OCR}(S)/OCR(S) \right)^2}{S = B, W}
\]  

(25)

8a) In the actual measurement of the "unknown" sample, the "actual elemental ratios" \( ARU(X) \), of the unknown element \( X \) are determined

\[
ARU(X) = \frac{I^+(X)}{I^+(Fe)}
\]

(26)

where individual ratios are calculated from each scan and proper averaging is performed over all scans analytical areas.

9a) "Corrected elemental Ratios" \( CRU(X) \) of the unknown element \( X \) are calculated:
The "relative elemental sensitivity factor" RSF (X) of the unknown element X (with respect to the matrix element Fe) is calculated according to

\[ RSF(X) = \frac{S_p(X)}{S_p(Fe)} = \frac{\frac{I^+(X)}{I^+(Fe)}}{c(X) / c(Fe)} = CRU(X) \cdot (c(Fe)/c(X)) \]  

The standard deviation of the RSF(X), \( \sigma_R(X) \), follows from (25)-(28):

\[ \sigma^2_R(X) = RSF(X) \left[ \frac{\sigma^2}{ARU(X)^2} \left( \frac{I^+(X)}{I^+(Fe)} \right) + \frac{\sigma^2}{RCF(\bar{M})^2} \right] \]  

for every unknown element X with mean mass number \( \bar{M} \).

5. Results

Fig. 2 and tab. 3 show practical sensitivities \( S_p \) as a function of atomic number for various elements X in B/Fe/X - samples. As expected from data obtained on other instruments /24/, /25/ sensitivity variations over a range of more than 2 orders of magnitude have been found. Absolute and relative practical sensitivities (referred to iron) of the d-shell metals show periodic atomic number dependence (Figs. 2 and 3): in the same period, the ion yield decreases with increasing atomic number, and in the higher periods the yields are lower in the same column.
Fig. 4 shows the influence of the third component on the practical sensitivities of the matrix elements B and Fe (upper two curves). Both, $S_p(B)$ and $S_p(Fe)$ are far from being independent of the admixture element but do not show a characteristic dependence, correlated to the atomic number of the admixture element. Only in the group Nb - Pd there seems to be a similar monotonous decrease of practical sensitivities for B and Fe with atomic number of admixture element X as is found in the practical sensitivities of the admixture elements themselves.

The lowest curve in fig. 4 shows the ratio $S_p(B)/S_p(Fe)$ (=: relative sensitivity factor of B with respect to Fe). This ratio shows a statistically significant (note the error bars!) dependence of the atomic number of the admixture element, even though its concentration is only 3 %. Obviously, the ion emission of B and Fe is influenced in a different manner by the third element present in the sample. Note, that the practical sensitivities of B and Fe (dotted lines) in the binary system B (16,6 %)/Fe, which most closely resembles the composition of the system B/Fe/X, are in the same range as in the ternary system and that the B/Fe ratio is generally increased in the ternary systems. Note also, that for the admixture elements studied absolute and relative practical sensitivities of the admixture elements themselves vary within a factor of about 200 (see figs. 2 and 3) that practical sensitivities of the matrix elements B and Fe, in dependence on the admixture element, vary within a factor of about 6 (fig. 4) and that the relative sensitivity of the matrix elements, again in dependence on the admixture element, varies only by a factor of about 2 (fig. 4).

As a comparison to the matrix effect caused by the 3 % admixture element, fig. 5 (and tabs. 3 and 4) show the dependence of B and Fe absolute and relative practical sensitivities in the three binary metallic glasses of the system B/Fe on the
relative fractional atomic concentration of boron. In fig. 5 the composition of the sample with c(B) = 16.6 at % corresponds to an eutectic mixture of B and Fe and most closely resembles the B/Fe ratio in the ternary systems described above. It can be seen, that the same factor of 2 - variation in the relative sensitivity factor of boron which maximally can be obtained by variation of a 3 % admixture element in the ternary system, requires a factor of 2 - variation of the boron concentration in the binary system.

In figs. 2-4 larger errors of the practical sensitivities $S_p$ than the respective ratios $S_p(X)/S_p(Fe)$ can partly be explained by long term drifts of the primary current $I_p$ which enters into all values of $S_p$ (see equs.(11), (12), (14)) but cancels out in the expression for the relative practical sensitivities (= relative sensitivity factors, see equ.(25)). Since the elemental mass ranges are always scanned in the sequence B-Fe-X, averaging in the former case is performed between experimental data taken at longer time intervals than in the latter case, thus reducing the influence of instrumental drift. By the same reason, relative sensitivity factors given in tab. 4 are not exactly identical to the appropriate ratios of the practical sensitivities from tab. 3.

6. Discussion

The atomic number dependence of the relative practical sensitivities (= relative sensitivity factors), measured in this work with a quadrupole mass spectrometer agree qualitatively and quantitatively reasonably well with data determined on magnetic sectorfield instruments /1/, /10/, /24/, /25/, /26/, using oxygen primary ions but somewhat different experimental
conditions (see tab. 5). These comparative data from the literature were obtained from polycrystalline, multicomponent low-concentration iron-based alloys /1/, /10/, or from pure element samples /25/, /26/, respectively. Fig. 3 in particular compares our data with the data from Storms et al. /25/. The agreement of these graphs would suggest, that, at least for the SOC of our quadrupole, given in tab. 1, no serious mass transmission bias against high masses is observed in the mass range investigated (10 - 190 amu). Note however that fig. 3 compares sensitivities of elements present as minor impurities in a metallic glass matrix (our work) with sensitivities determined from the pure elements (Storms et al.´s work /25/). Therefore, it cannot be completely excluded, that the B/Fe matrix "smoothes out" the variability in the ion yields between elements so that even in a quadrupole with low transmission at high mass numbers high apparent yields for the heavy elements would be observed. The observation however, that in our measurements the relative yield variations within one group of the periodic system (e.g. Nb-Pd, Ta-Ir) is of the same order as in the measurements of Storms et al. /25/ speaks against this possibility. Nevertheless, there remain some significant differences in relative yields of individual elements (e.g. Mn/Ni, Nb/Mo, Os) which cannot be explained at the moment.

The absolute values of the practical sensitivities, determined by Storms et al. are about 2 orders of magnitude higher than our values. The dominant reason for this reduced sensitivity appears to be the lower transmission of the quadrupole, when compared to a sectorfield instrument. As has been pointed out in section 4, the transmission of our quadrupole can be increased in a limited mass range by more than one order of magnitude, when instrument adjustments are optimized for that range. A general reduction of ion yields of the admixture elements X compared to the pure elements X appears to be unlikely when the factor of 100 - difference in the practical sensitivity of Fe
(comparing our value $S_p(\text{Fe}) = 3.8 \cdot 10^3 \text{ cps/nA}$ with Storms et al.'s value $S_p(\text{Fe}) = 3.8 \cdot 10^5 \text{ cps/nA}$) is seen in conjunction with the absence of large systematic mass discrimination effects in our quadrupole (using the SOC of tab. 1).

The relative and absolute practical sensitivities of the matrix elements B and Fe are also marked in figs. 2 and 3 and compared to the corresponding data of the admixture elements. The values are reasonably fitting the trend within the respective group of the periodic system, although B seems to be a little low when compared to the results of Storms et al. Another interesting fact is, that absolute and relative practical sensitivities, determined for trace elements in borated stainless steel (VEW; A 978 Sc/melt 147504; 17 wpc Cr, 12.6 wpc Ni, 1.5 wpc B) are in good agreement with the sensitivities of the same elements in the Fe-B-X metallic glass system; also, $S_p(B)$, as determined from boron, ion implanted into silicon, is in reasonable agreement with $S_p(B)$ from metallic glass and stainless steel (see figs. 2 and 3). The same operating conditions and the same data evaluation procedure as described in section 4 was followed in the determination of the practical sensitivities in stainless steel and ion-implanted silicon. Obviously, at least for the elements shown in fig. 3, relative sensitivity factors determined in the B/Fe/W system could also be used to quantify trace elements in stainless steel by means of the RSF quantitation method /27/, /1/. An average analytical accuracy of the order of $\pm 30\%$ can be expected in this procedure.

In the three-component alloys element X is emitted in each case from the same matrix: the neighbourhood of one X-atom contains about 27 Fe- and 6 B-atoms because of the random composition of the amorphous state. Therefore, the ion yields of the X-atoms can be directly compared, because the matrix effect is identical in all the different ternary alloys studied in
this work. In the two-component alloys the absolute and relative practical sensitivity of boron increases with increasing iron content, while the boron concentration does not change the ion yield of Fe significantly (fig. 5). According to the DRPHS model it is supposed that no two metalloid atoms could be nearest neighbours /28/, which means that in the emission process not only the nearest neighbour atoms interact.

In the ternary alloys the influence of the matrix (the changing nature of the X element) generally causes only a weak matrix-effect on the emission of iron and boron (fig. 4). This is in good agreement with Smith’s and Christie’s measurements with 5 different iron-based alloys /1/ according to which, in the range of low concentration, the mutual matrix-effect of the constituents is generally less than a factor of 1.5. Nevertheless, some trends in the matrix-effect can be observed. The practical sensitivity of Fe is generally decreases and that of B is mostly increased by the metal X. In the two-component alloys, an increasing Fe-content also increases $S_{\text{Fe}}(B)$. Some recent publications about high concentration alloys /29/, /2/ render it probable that in the binary homogeneous alloys the element of higher ionisation probability increases the practical sensitivity of the other metal, while the latter one can have a reverse influence on the previous one. The present results correlate with the following observation: the low sensitivity of boron is increased by the admixture of V, Fe, Mn, Co, Ni, Nb, Mo (metals with higher sensitivity) decreased by Os, Ir (metals with lower sensitivity). The sensitivity of Fe is increased by Nb and decreased by Ru, Rh, Pd, Ta, Os, Ir. The number of exceptions however is large.

7. Conclusion

Absolute and relative practical sensitivities under oxygen
primary ion bombardement of 14 elements, contained as 3 at % admixture in the metallic glass system Fe$_{80}$B$_{17}$ have been determined. During the course of these measurements a method ("PCS" - method) had to be developed for tuning a SIMS instrument so that reproducible spectra are always obtained from the same sample. The PCS algorithm compensates for instrument drift and increases reproducibility and analytical accuracy of the results. Taking into account all statistical and systematic errors, relative sensitivity factors were determined with a standard deviation ($\sigma$ ) ranging from 2 % to 40 % (for the extreme low yield elements).

The variations in absolute and relative practical elemental sensitivities measured in this work on a quadrupole instrument agrees qualitatively and quantitatively reasonably well with data obtained on double focusing sectorfield instruments indicating, that for the operating conditions used in this work, systematic mass discrimination effects of the quadrupole mass filter are minimized. In the ternary systems the 3 % admixture element causes a small but statistically significant matrix effect in the sensitivities of the matrix elements Fe and B; the boron sensitivity is generally increased by the admixture of elements with higher sensitivity and decreased by admixture of elements with lower sensitivity than boron.

Comparison of absolute and relative elemental sensitivities from the metallic glass matrix with those from other matrix types (stainless steel, ion implanted Si) shows that, for the elements measured in this work at least, all elements lie within a factor of 2 and most elements within 30 %. This opens the possibility to quantify SIMS spectra from other Fe-based alloys using relative sensitivity factors obtained on metallic glass standards. These standards are preferable to frequently used polycrystalline standards due to their spatial homogeneity, the increased range of concentrations forming a single phase system and due to the great number of elements forming homogeneous metallic glass phases.
References

/2/ M. Riedel: Theses (1978) Budapest
/9/ F.G. Rüdenauer, J.Giber; Contact Seminar TU Vienna/TU Budapest; Vienna (1981); unpublished
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/19/ F.G. Rüdenauer, W. Steiger and U. Kraus, Microchim Acta (Wien) Suppl 8 (1979) 51
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/22/ A. Benninghoven, F.G. Rüdenauer and H.W. Werner, to be published
/23/ J. Maul, GSF-Ber. P74; Ges. f. Strahlen- und Umweltforschung, D-8042 Neuherberg, W-Germany
/24/ H.E. Beske, Zeitschr. f. Naturforschg. 22a (1967) 459
Table 1 Standard Operating Conditions (SOC) for Fe-B-W Metallic Glass System

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary ions</td>
<td>10 keV, $^{16}\text{O}_2^+$, mass filtered</td>
</tr>
<tr>
<td>Primary ion current</td>
<td>ca. 20 nA</td>
</tr>
<tr>
<td>Beam diameter</td>
<td>ca. 50 μm</td>
</tr>
<tr>
<td>Angle of incidence</td>
<td>$0^\circ$ with respect to target normal</td>
</tr>
<tr>
<td>Residual gas pressure in sample chamber</td>
<td>$&lt; 2 \times 10^{-8}$ mbar</td>
</tr>
<tr>
<td>Oxygen bleeding</td>
<td>no</td>
</tr>
<tr>
<td>Presputter raster</td>
<td>200 x 200 μm, 10 min</td>
</tr>
<tr>
<td>Analytical raster</td>
<td>100 x 100 μm</td>
</tr>
<tr>
<td>Secondary ion takeoff</td>
<td>45°</td>
</tr>
</tbody>
</table>

**Standard Quadrupole Settings:**

**ESX 156 (energy preselector):**

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<th>Component</th>
<th>Setting</th>
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</thead>
<tbody>
<tr>
<td>Ext. Defl. P1</td>
<td>-34.5 volt</td>
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<tr>
<td>Int. Defl. P2</td>
<td>-157.7 &quot;</td>
</tr>
<tr>
<td>Accel. Lens P3</td>
<td>-31.2 &quot;</td>
</tr>
<tr>
<td>Input Lens P4</td>
<td>-69.4 &quot;</td>
</tr>
</tbody>
</table>

**DPX 156 (focusing lenses):**

<table>
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<th>Setting</th>
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</thead>
<tbody>
<tr>
<td>Input Foc. 1</td>
<td>-181.2 volt</td>
</tr>
<tr>
<td>Input Foc. 2</td>
<td>-162.0 &quot;</td>
</tr>
<tr>
<td>Input Foc. 3</td>
<td>+15.9 &quot;</td>
</tr>
<tr>
<td>Filter Inp. 4</td>
<td>-99.3 &quot;</td>
</tr>
<tr>
<td>Prefilter 5</td>
<td>-10.0 &quot;</td>
</tr>
<tr>
<td>Output Foc. 6</td>
<td>+28.1 &quot;</td>
</tr>
<tr>
<td>Deviation 7</td>
<td>-89.0 &quot;</td>
</tr>
<tr>
<td>Deviation 8</td>
<td>-25.8 &quot;</td>
</tr>
</tbody>
</table>

**AQ 156 (rod supply):**

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<th>Setting</th>
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</thead>
<tbody>
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<td>Accord</td>
<td>678 (Potentiometer)</td>
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<tr>
<td>LM Res.</td>
<td>65 &quot;</td>
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<tr>
<td>LM Pol.</td>
<td>07 &quot;</td>
</tr>
<tr>
<td>HM Res.</td>
<td>512 &quot;</td>
</tr>
<tr>
<td>HM Pol.</td>
<td>520 &quot;</td>
</tr>
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</table>
Table 2 Original Yield data, under Standard Operating Conditions, for metallic glass sample Fe$_{80}$B$_{17}$W$_3$

<table>
<thead>
<tr>
<th></th>
<th>Value (cps/nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAY(B)</td>
<td>$380 \pm 22$</td>
</tr>
<tr>
<td>OAY(FE)</td>
<td>$3150 \pm 190$</td>
</tr>
<tr>
<td>OAY(W)</td>
<td>$37.9 \pm 4.6$</td>
</tr>
<tr>
<td>OCR(B)</td>
<td>$1.21 \cdot 10^{-1} \pm 6.0 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>OCR(W)</td>
<td>$1.20 \cdot 10^{-2} \pm 9.3 \cdot 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 3 Practical sensitivities of elements in binary and ternary metallic glasses of the composition Fe$_{80}$B$_{17}$X$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_p(B)$ (cps/nA)</th>
<th>$S_p(Fe)$ (cps/nA)</th>
<th>$S_p(X)$ (cps/nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe B 11.7 %</td>
<td>1860 ± 260</td>
<td>3810 ± 420</td>
<td>----</td>
</tr>
<tr>
<td>Fe B 16.6 %</td>
<td>1310 ± 160</td>
<td>3640 ± 450</td>
<td>----</td>
</tr>
<tr>
<td>Fe B 21.6 %</td>
<td>1280 ± 150</td>
<td>4090 ± 410</td>
<td>----</td>
</tr>
<tr>
<td>Fe B V</td>
<td>1526 ± 87</td>
<td>3310 ± 200</td>
<td>6620 ± 520</td>
</tr>
<tr>
<td>Fe B Cr</td>
<td>1380 ± 210</td>
<td>2670 ± 260</td>
<td>7360 ± 740</td>
</tr>
<tr>
<td>Fe B Mn</td>
<td>1490 ± 160</td>
<td>3630 ± 240</td>
<td>6350 ± 370</td>
</tr>
<tr>
<td>Fe B Co</td>
<td>2130 ± 290</td>
<td>4590 ± 450</td>
<td>3900 ± 370</td>
</tr>
<tr>
<td>Fe B Ni</td>
<td>1630 ± 370</td>
<td>4140 ± 650</td>
<td>2370 ± 500</td>
</tr>
<tr>
<td>Fe B Nb</td>
<td>2820 ± 580</td>
<td>5700 ± 970</td>
<td>17300 ± 4400</td>
</tr>
<tr>
<td>Fe B Mo</td>
<td>1690 ± 210</td>
<td>3280 ± 310</td>
<td>5800 ± 740</td>
</tr>
<tr>
<td>Fe B Ru</td>
<td>1250 ± 290</td>
<td>3360 ± 1000</td>
<td>2750 ± 760</td>
</tr>
<tr>
<td>Fe B Rh</td>
<td>1314 ± 68</td>
<td>3210 ± 170</td>
<td>1898 ± 95</td>
</tr>
<tr>
<td>Fe B Pd</td>
<td>1340 ± 250</td>
<td>3570 ± 390</td>
<td>575 ± 91</td>
</tr>
<tr>
<td>Fe B Ta</td>
<td>1150 ± 190</td>
<td>3160 ± 320</td>
<td>2000 ± 720</td>
</tr>
<tr>
<td>Fe B W</td>
<td>2240 ± 130</td>
<td>3930 ± 240</td>
<td>1260 ± 160</td>
</tr>
<tr>
<td>Fe B Os</td>
<td>870 ± 150</td>
<td>2650 ± 380</td>
<td>197 ± 77</td>
</tr>
<tr>
<td>Fe B Ir</td>
<td>1170 ± 140</td>
<td>3220 ± 390</td>
<td>67 ± 31</td>
</tr>
</tbody>
</table>
Table 4 Relative Practical Sensitivities (Relative Sensitivity Factors, RSF) with respect to Fe of elements in binary and ternary metallic glasses of the composition Fe$_{80}B_{17}X_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_p(B)/S_p(Fe)$</th>
<th>$S_p(X)/S_p(Fe)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe B 11.7 %</td>
<td>0.506 ± 0.008</td>
<td></td>
</tr>
<tr>
<td>Fe B 16.6 %</td>
<td>0.375 ± 0.024</td>
<td></td>
</tr>
<tr>
<td>Fe B 21.6 %</td>
<td>0.307 ± 0.009</td>
<td></td>
</tr>
<tr>
<td>Fe B V</td>
<td>0.445 ± 0.007</td>
<td>2.000 ± 0.050</td>
</tr>
<tr>
<td>Fe B Cr</td>
<td>0.529 ± 0.040</td>
<td>2.723 ± 0.007</td>
</tr>
<tr>
<td>Fe B Mn</td>
<td>0.423 ± 0.014</td>
<td>1.751 ± 0.018</td>
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<tr>
<td>Fe B Co</td>
<td>0.457 ± 0.020</td>
<td>0.844 ± 0.016</td>
</tr>
<tr>
<td>Fe B Ni</td>
<td>0.443 ± 0.022</td>
<td>0.602 ± 0.016</td>
</tr>
<tr>
<td>Fe B Nb</td>
<td>0.515 ± 0.024</td>
<td>3.187 ± 0.231</td>
</tr>
<tr>
<td>Fe B Mo</td>
<td>0.525 ± 0.013</td>
<td>1.758 ± 0.053</td>
</tr>
<tr>
<td>Fe B Ru</td>
<td>0.374 ± 0.031</td>
<td>0.830 ± 0.110</td>
</tr>
<tr>
<td>Fe B Rh</td>
<td>0.406 ± 0.002</td>
<td>0.587 ± 0.008</td>
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<tr>
<td>Fe B Pd</td>
<td>0.378 ± 0.041</td>
<td>0.168 ± 0.017</td>
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<tr>
<td>Fe B Ta</td>
<td>0.389 ± 0.026</td>
<td>0.605 ± 0.044</td>
</tr>
<tr>
<td>Fe B W</td>
<td>0.570 ± 0.003</td>
<td>0.320 ± 0.025</td>
</tr>
<tr>
<td>Fe B Os</td>
<td>0.363 ± 0.007</td>
<td>0.076 ± 0.011</td>
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<tr>
<td>Fe B Ir</td>
<td>0.379 ± 0.037</td>
<td>0.018 ± 0.007</td>
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</table>
Table 5  Relative sensitivity factors (RSF) in Fe-based alloys using oxygen-ion bombardment

<table>
<thead>
<tr>
<th>Period</th>
<th>Metal</th>
<th>this work</th>
<th>Smith et al.</th>
<th>Schroer</th>
<th>Storms et al.</th>
<th>Andersen</th>
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<tr>
<td></td>
<td></td>
<td>e)</td>
<td>/1/, a)</td>
<td>/10/, b)</td>
<td>/24/, c)</td>
<td>/25/, d)</td>
</tr>
<tr>
<td>2 d</td>
<td>B</td>
<td>0.38</td>
<td>0.15</td>
<td>?</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>3 d</td>
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? .... error of determination > factor 2
a) IMMA; 15 keV; $O_2^+$; $p = 10^{-6}$ torr
b) AEI; 15 keV; $O_2^+$; $p = 3 \times 10^{-7}$ torr
c) IMMA; 13.5 keV; $O^-$; $p = 10^{-7}$ torr
d) IMMA; 11 keV; $O^-$
e) RIBER Quadrupole; 10 keV, $O_2^+$; $p = 2 \times 10^{-8}$ torr
Table 6 Subdeterminants $D_1 \ldots D_9$ of determinant $\Delta$ for the general case

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<tr>
<th></th>
<th>$D_1$</th>
<th>$D_2$</th>
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<th>$D_6$</th>
<th>$D_7$</th>
<th>$D_8$</th>
<th>$D_9$</th>
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<td>$(\overline{M}_1 - M_c) (\overline{M}_1 - M_c)^2$</td>
<td>$(\overline{M}_2 - M_c) (\overline{M}_2 - M_c)^2$</td>
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The subdeterminants $D_1 \ldots D_9$ are defined as follows:

- $D_1 = (\overline{M}_2 - M_c) (\overline{M}_2 - M_c)^2$ for the general case.
- $D_2 = (\overline{M}_1 - M_c) (\overline{M}_1 - M_c)^2$.
- $D_3 = (\overline{M}_2 - M_c) (\overline{M}_2 - M_c)^2$.
- $D_4 = 1 (\overline{M}_2 - M_c)^2$.
- $D_5 = 1 (\overline{M}_1 - M_c)^2$.
- $D_6 = 1 (\overline{M}_2 - M_c)^2$.
- $D_7 = 1 (\overline{M}_1 - M_c)^2$.
- $D_8 = 1 (\overline{M}_1 - M_c)^2$.
- $D_9 = 1 (\overline{M}_1 - M_c)^2$. 
Captions to Figures

Fig. 1 Interpolation of yield correction factor $Y_{CF}(\bar{M})$ between elements contained in the primary calibration standard (B, Fe, W).

Fig. 2 Practical Sensitivities of elements from metallic glass matrices $\text{Fe}_{80}\text{B}_{17}\text{X}_3$ and other matrix types.

Fig. 3 Relative practical sensitivities (referred to Fe) of elements form metallic glass matrices $\text{Fe}_{80}\text{B}_{17}\text{X}_3$ and stainless steel compared to data of Storms et al. /24/ from pure elements.

Fig. 4 Absolute and relative practical sensitivities of matrix elements in metallic glasses $\text{Fe}_{80}\text{B}_{17}\text{X}_3$ for various 3 at % admixture elements (matrix effect).

Fig. 5 Absolute and relative practical sensitivities of Fe and B in binary Fe-B metallic glasses.
Fig. 1
Fig. 2
Fig. 4
Fig. 5
QEFZS-Berichte

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