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Efficient mass calibration of magnetic sector mass spectrometers

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Abstract: Magnetic sector mass spectrometers used for automatic acquisition of precise isotopic data are usually controlled with Hall probes and software that uses polynomial equations to define and calibrate the mass-field relations required for mass focusing. This procedure requires a number of reference masses and careful tuning to define and maintain an accurate mass calibration. A simplified equation is presented and applied to several different magnetically controlled mass spectrometers. The equation accounts for nonlinearity in typical Hall probe controlled mass-field relations, reduces calibration to a linear fitting procedure, and is sufficiently accurate to permit calibration over a mass range of 2 to 200 amu with only two defining masses. Procedures developed can quickly correct for normal drift in calibrations and compensate for drift during isotopic analysis over a limited mass range such as a single element. The equation is:

$$\text{Field} = A \cdot \text{Mass}^{1/2} + B \cdot (\text{Mass})^{p}$$

where A, B, and p are constants. The power value p has a characteristic value for a Hall probe/controller and is insensitive to changing conditions, thus reducing calibration to a linear regression to determine optimum A and B.

Résumé : Les spectromètres de masse à secteur magnétique fonctionnent habituellement avec des sondes Hall et un logiciel qui se sert d'équations polynomiales pour définir et étalonner les relations masse-champ requises pour la focalisation de masse. Ces appareils sont utilisés pour l'acquisition automatique de données isotopiques précises. Ils nécessitent plusieurs masses de référence et un ajustement précis pour définir et maintenir un étalonnage exact de la masse. Une équation simplifiée est présentée et appliquée à plusieurs spectromètres de masse contrôlés magnétiquement. Cette équation tient compte de la non linéarité des relations typiques entre la masse et le champ qui sont contrôlées par la sonde, réduit l'étalonnage à un ajustement linéaire et est suffisamment exacte pour permettre un étalonnage sur un intervalle de masse de 2 à 200 amu en n'utilisant que deux masses de définition. Les procédés élaborés servent à corriger rapidement l'écart normal observé dans les étalonnages et à compenser l'écart durant l'analyse isotopique sur un intervalle de masse limité comme dans le cas d'un seul élément. L'équation est la suivante :

$$\text{champ} = A \cdot \text{masse}^{1/2} + B \cdot (\text{masse})^{p}$$

où A, B et p sont des constantes. La valeur de la puissance (p) est caractéristique pour une sonde Hall et ne varie pas avec les conditions changeantes, ce qui réduit l'étalonnage à une régression linéaire visant à déterminer les valeurs optimales de A et de B.

[1] Deceased

INTRODUCTION

Mass spectrometer manufacturers now provide sophisticated computer software to control the various functions of, and data collection from, their instruments. To control the magnet for focusing the required masses on ion beam detectors, it is usual for the software to use a third degree or higher polynomial equation to define the mathematical relation between the mass and magnetic field as measured by a Hall probe. Calibration of this polynomial relation requires the determination of the intensity of the magnetic field for at least three masses over the mass range of interest. Because of the nonlinearity of the relation of mass to field intensity, a larger number of calibrating masses over the complete mass range will provide a more precise calibration. This requirement of a number of defining masses over a large mass range results in a calibration needing special samples with the appropriate range of isotopes to encompass the mass range. Defining each isotope for calibration involves varying the magnetic field in the appropriate mass range for an element and then confirming the correct isotope by identifying the relative abundances of the isotopes for that element. With changes in operating parameters or drift in instrument conditions a new calibration must be carried out. Therefore significant amounts of time may be spent in maintaining a precise and accurate calibration of the mass scale of the instrument. Here, an alternative algorithm to the polynomial equation is presented. Using this algorithm, calibration of the magnetic field is significantly simplified and maintenance can be reduced to a re-calibration using a single mass. The procedure appears to have general applicability to magnetic sector instruments controlled with Hall probes and is demonstrated for several different mass spectrometers.

DEVELOPMENT OF A MASS-FIELD ALGORITHM

The development of improved mass calibration of mass spectrometers was first carried out on a Finnigan-MAT 261 thermal ionization instrument at the Geological Survey of Canada. Application of the algorithm to several other MAT 261 machines confirmed the general applicability of calibration to this type of machine. Subsequently the algorithm was used to calibrate a VG 3600 gas mass spectrometer and a NBS Shields design 12", 90 magnetic sector thermal ionization mass spectrometer controlled with Teslameters recently developed by the National Institute of Standards and Technology (NIST). All these instruments use Hall probes to measure and control the magnetic field. Calibration of the VG 3600 is used for development of the algorithm and the applicability to other instruments demonstrates the usefulness of the algorithm in the calibration of different mass spectrometers.

The equation relating mass (m) to magnetic flux density (F) for mass spectrometers which use magnetic field switching of a magnet (radius r) to accelerate particles of charge q through an electric field of V volts is

$$2 \cdot m \cdot V = F^2 \cdot q \cdot r^2 \qquad (1)$$

The high voltage is normally maintained at a constant value and for particles of mass to charge ratio M (=m/q) the basic relation simplifies to

$$F = A \cdot M^{1/2} \qquad (2)$$

where A is a constant. Therefore the field required to focus an isotope on a detector should be a linear function of the square root of mass and determination of the field at a single mass will define the constant A and thus the field values at all other masses. If the observed relation of mass to field, as measured and controlled by a Hall probe, follows this relation calibration is a trivial exercise. Unfortunately, this is not the case and thus polynomial fits have been applied to the calibration of mass spectrometers. In some cases these fits may use the mass versus observed field and not the root mass versus field data which are relatively linear (Fig. 1).

Table 1 presents measured magnetic field intensity of a VG 3600 mass spectrometer over the mass range ^{2}H to ^{186}W. A number of masses are multiple charge W isotopes from the filament in the mass spectrometer. The observed magnetic field values are expressed as volts of output from

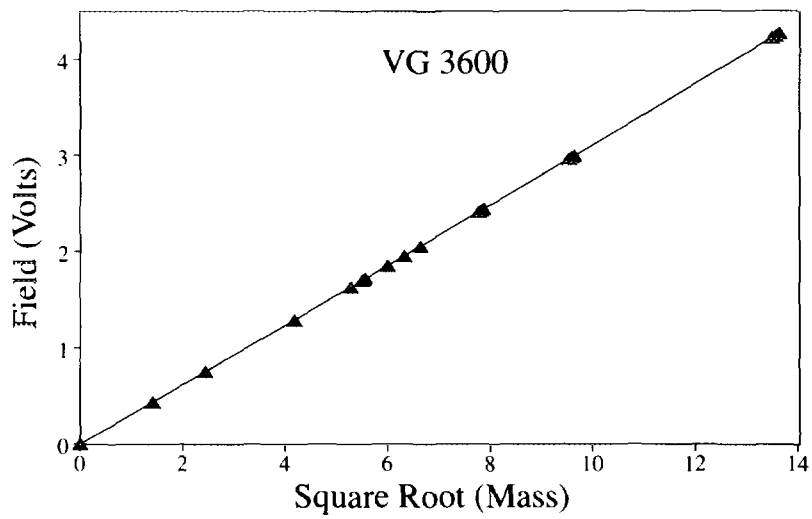

Figure 1.

A plot showing the apparent linearity of the variation of magnetic field intensity with the square root of mass for a VG 3600 mass spectrometer as expected from Equation 2. The field is expressed as a voltage output from a Hall probe. The data are from Table 1.

Table 1. Measured magnetic field in volts from a Hall probe versus mass for a VG 3600 mass spectrometer.

Isotope	Charge	Mass M	Measured Field F in Volts	A= F/M
---		0		0.3074*
$^{1}H_2$	+	2.0157	0.43657	0.3075
^{12}C	2+	6.0000	0.75444	0.3080
^{35}Cl	2+	17.484	1.29062	0.3087
^{28}N	+	28.006	1.63461	0.3089
^{182}W	6+	30.325	1.70181	0.3090
^{184}W	6+	30.659	1.71140	0.3091
^{186}W	6+	30.992	1.72098	0.3091
^{36}Ar	+	35.968	1.85449	0.3092
^{40}Ar	+	39.962	1.95544	0.3093
$^{12}C^{16}O_2$	+	43.990	2.05320	0.3096
^{182}W	3+	60.649	2.41470	0.3101
^{184}W	3+	61.317	2.42820	0.3101
^{186}W	3+	61.985	2.44150	0.3101
^{182}W	2+	90.974	2.96647	0.3110
^{184}W	2+	91.976	2.98321	0.3111
^{186}W	2+	92.977	2.99990	0.3111
^{182}W	+	181.948	4.22808	0.3135
^{184}W	+	181.951	4.25222	0.3135
^{186}W	+	181.954	4.27611	0.3136

*Extrapolated value

the instrument's Hall probe. Figure 1, a mass versus field plot for these data, displays an apparently linear relation as expected from the theoretical equation (Equation 2). Table 1, however, shows that the relation is not precisely linear as the ratio of F/M (= A) ranges from 0.3075 to 0.3136, a variation of about 2% over the tabulated mass range. A precise mass calibration must correct for this small deviation from the theoretical relation. An estimate of a limiting value of A may be made by extrapolating the variation of A in Table 1 to zero mass. Using this zero mass value of A, Figure 2A shows that the deviation of the observed field from the theoretical field based on Equation 2 is a regular positive variation with mass. Addition of a function to Equation 2 which corrects for this deviation from the theoretical function will better define the observed mass-field relation tabulated in Table 1 and provide a linear calibration procedure.

The correcting function must model the curve of Figure 2A which shows an increasing field deviation with increasing mass, and can be accommodated for by making the correction proportional to mass raised to a power p that is greater than 1.0. Therefore the correcting function approximating the curve of Figure 2 can be written as $B \cdot M^p$ where B is a constant. The power factor p will account for any curvature of the correcting function and simplifies to a linear correction with mass if p = 1.0. Modelling this relation to

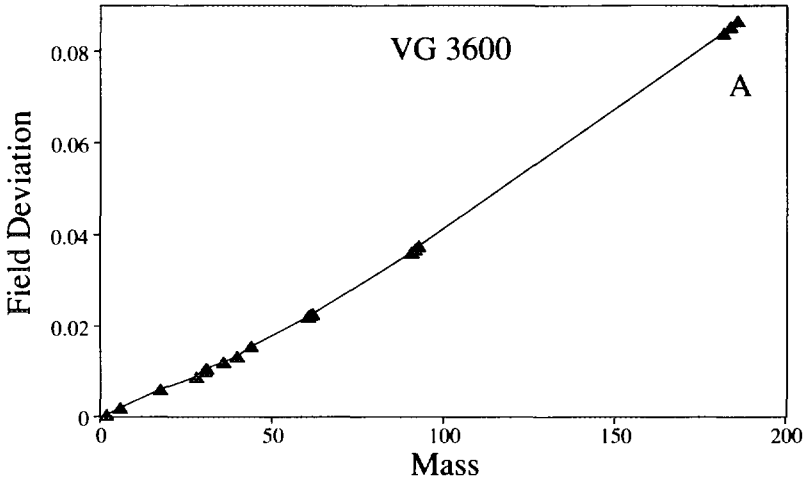

Figure 2A.

The deviations of observed magnetic field intensity (Table 1) from theoretical values defined by the relation of Equation 2 (F = A·M) for a VG 3600 mass spectrometer. The deviations, in units of volts, are slightly nonlinear with mass with increasingly positive values of up to 2.0% greater than the theoretical field at mass 186.

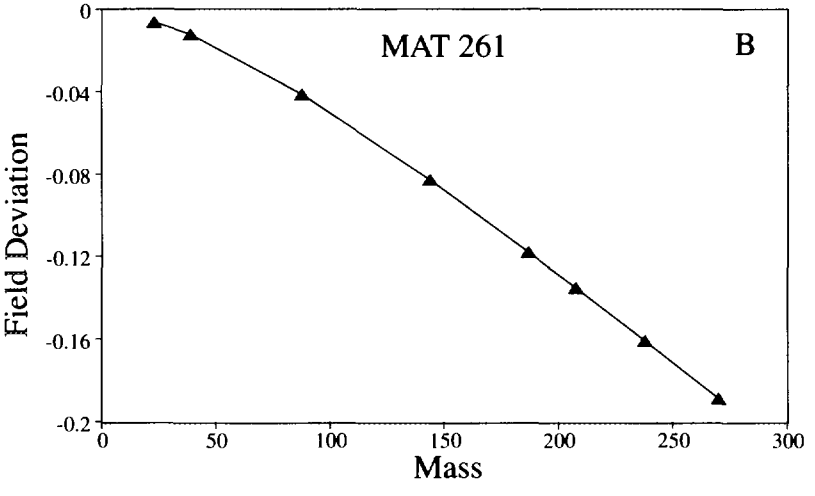

Figure 2B.

A plot similar to Figure 2A for a Finnigan-MAT 261 mass spectrometer at eight field values at masses 23, 39, 88, 144, 187, 208, 238, and 270. The field intensity is scaled to the same units and intensity as the VG 3600 data at mass 186 to permit comparison of deviations of the different mass spectrometers. In this case the deviations (in volts) are increasingly negative with -2.7% deviation from the theoretical field at mass 187.

determine the appropriate B and p which fit the curve of Figure 2A shows that values of B = 0.00016 and p = 1.25 are best but the sensitivity to p is not great and p can have values ranging from 1.15 to 1.30 with appropriate compensating values of A and B. Finnigan-MAT 261 mass spectrometers show a similar nonlinear deviation but with an increasingly negative deviation from the theoretical field with increasing mass (Fig. 2B). The appropriate power factor p, however, is similar to the VG 3600 data with values from 1.0 to 1.3, and typically 1.2.

The general equation defining the observed mass-field relation is therefore:

$$F = A \cdot M^{1/2} + B \cdot M^{p} \quad (3)$$

where p = 1.2 (typical).

The second term is a correction to restore linearity in the F versus M relation. This equation can be rearranged to define a linear function and regression analysis applied to a set of calibration data to determine the best values of the parameters A and B with p at a suitable fixed value. Rewriting Equation 3 as

$$F/M^{1/2} = A + B \cdot M^{p-0.5} \quad (4)$$

an equation of a straight line is defined with a slope of B and an intercept of A. Figure 3A presents the results of applying regression analysis to the VG 3600 data in Table 1 with the per cent deviations of the observed field from the regression line plotted against mass. The deviations are generally less than 0.03% over the mass range from 2 to 186 amu, with a ±0.002% reproducibility of field values using a beam centring routine. These deviations can be compared to the precision necessary to focus an ion beam in the detector. The VG3600 has a resolution of 300 at 5% peak height which is equivalent to requiring the field to be within ±0.085% of the correct value to collect 5% of the peak. Collector slit width is set to permit collection of all the ion beam arriving at the slit for a ±0.040% variation of the field and this results in a flat topped region of the peak. Therefore over the mass range 2-186 amu the algorithm can focus on 5% of a peak and in most cases focus on the maximum or flat topped region of a peak. The masses with field deviations of 0.05-0.06% will be positioned on >50% of a peak and can be subsequently centred. Magnet hysteresis may be responsible for some of the observed scatter as no attempt was made to determine the mass-field values in a systematic manner (i.e. with increasing field). Note that if mass is to be determined the equivalent per cent deviations of mass from the regression line are double the field deviations because mass is dependent on the square of the field (Equation 1). Sensitivity to the power factor p is shown in Figure 3B where the same analysis is applied using p = 1.25. There is a slight improvement in the fit of most masses over the mass range defined.

Figure 4 presents the same analysis as above to data from two Finnigan-MAT 261 mass spectrometers. The plot with a power factor p = 1.25 is the same data as displayed in Figure 2B. The fit of the data is similar to that of the VG 3600 with the three lowest masses deviating by ±0.03-0.06% (with ±0.001% reproducibility) but the remaining masses are in

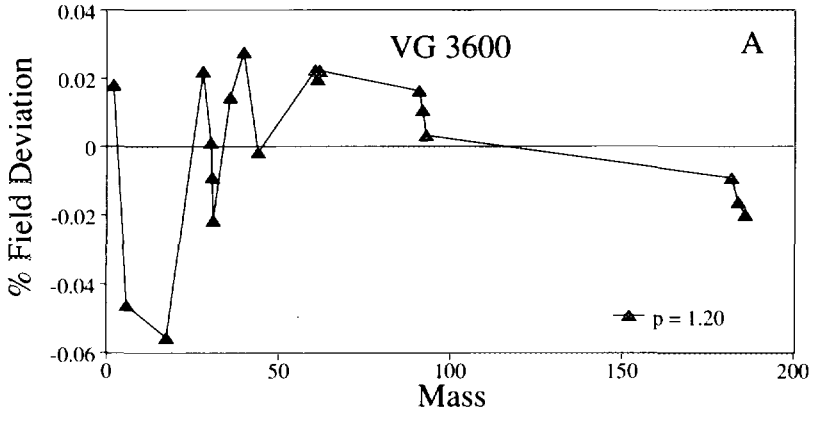

Figure 3A.

A plot of deviations of observed magnetic field intensities from calculated values based on applying Equation 3 to VG 3600 data of Table 1. Reproducibility of the field values is about 0.002% using a beam centring routine. Deviations of <±0.040% will accurately focus a mass in the ion detector. The deviations are derived from regression of the data calculated using Equation 4 with p = 1.2 and result in parameters of A = 0.30729, B = 0.000160.

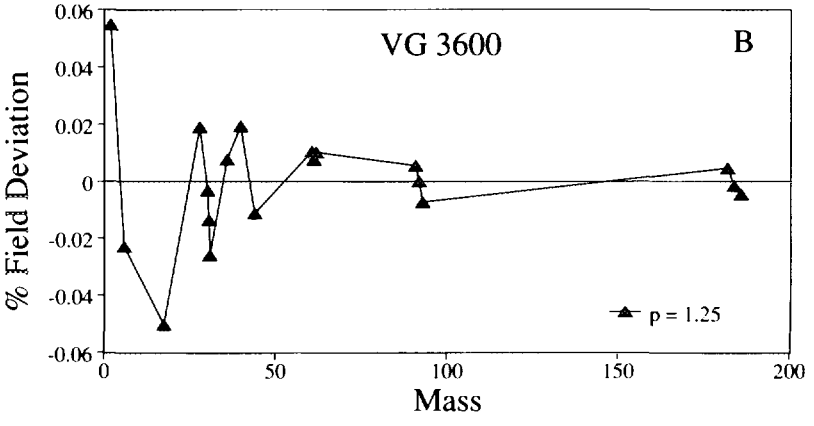

Figure 3B.

Plot of the same data as Figure 3A but with a regression using p = 1.25. This regression results in parameters of A = 0.30746, B = 0.000121.

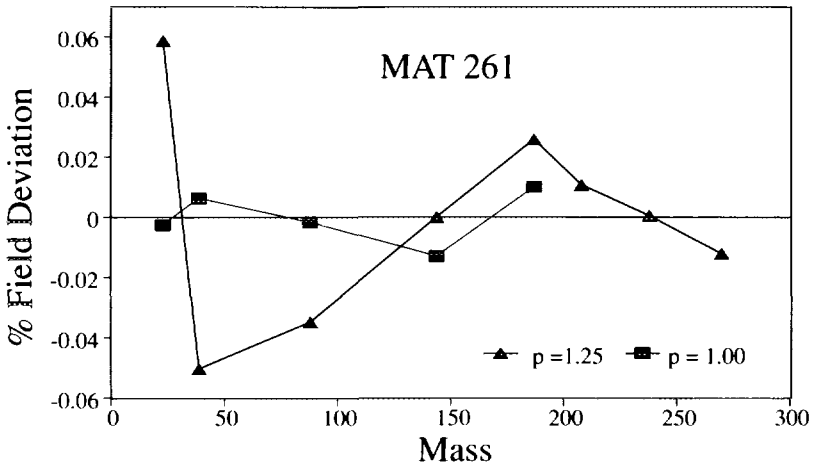

Figure 4.

A similar plot to Figure 3 for data from two Finnigan-MAT 261s. The per cent deviations for the data with p = 1.25 are derived from a regression of the eight observations in Figure 2B, calculated using Equation 4 with p = 1.25 and result in parameters of A = 0.32303, B = -0.000185. The second data set is from another MAT 261 with an optimum power factor p = 1.0 for the mass range 23 to 187 amu. Regression results are A = 0.33138 and B = -0.00130.

better agreement. This instrument has a 5% resolution of 500, equivalent to a field uncertainty of ±0.050% for detecting 5% peak intensity and a peak flat topped region of ±0.018% of field. Therefore over the mass range 23-270, the mass calibration will focus on 5% of a required mass, and for masses 100-270 on or near the optimum region of a peak. The second data set with a mass range of 23 to 187 is from another MAT 261 with an optimum power factor of p = 1.0, indicating a linear deviation with mass from the ideal relation. In this case all field values are within the range required to focus on the flat topped peak region.

Figure 5 presents similar results for a NBS Shields 12" mass spectrometer controlled with two different Hall probe based NIST Teslameters. In the case of Teslameter #1 the magnitude of the observed deviations from the theoretical relation (Fig. 5A) are similar to the MAT 261 (Fig. 2B) but with greater curvature of the relation. For this instrument a larger power factor p of 1.7 is required to correct for the curvature. Figure 5B shows that regression analysis of the mass-field values fit to within 0.06% for all but masses 23 and 39 which deviate by ±0.10%. In contrast, calibration with Teslameter #2 shows about 18 times less deviation from the theoretical relation (Fig. 5A) and very little curvature to the correcting relation (optimum p = 0.35). The fit of the data also is improved with calculated field values within ±0.020% of the observed values (Fig. 5B). The relation is insensitive to the power factor for Teslameter #2 and for a regression using p = 1.0 the deviations remain within ±0.020% of observed values. This instrument, with a 5% resolution of 315, is similar to the VG3600, and therefore requires a field uncertainty of ±0.085% for detecting 5% peak intensity. The peak flat topped region is ±0.040% of field. Therefore over the mass range 23-270, a calibration using Teslameter #2 can focus on the optimum field for all masses. In contrast, for Teslameter #1 the mass calibration will focus on 5% intensity of a required mass for masses greater than 50 but at masses 23 and 39 the deviations are significant enough that a peak could be missed.

APPLICATION OF THE ALGORITHM TO MASS CALIBRATION AND ANALYSES

The use of the mass-field calibration algorithm for routine analyses can be applied in several ways. If the magnet and electronics are very stable there will be little or no change of calibration with time and a detailed mass-field reference table, such as Table 1 for the VG 3600, can be established. The parameters A and B of Equation 3 could be determined once and a recalibration carried out if any mass is found to be drifting significantly from the calculated field value. Minor drift can be corrected in a simple manner. Because of the nearly linear relation of field with square root of mass (Fig. 1), to a very good approximation field drift arising from electronic drift, or minor magnet repositioning for optimum peak shape, involves a small change of slope of the curve and a change in all calibrated field values by the same fractional or percentage amount. Thus a small fractional drift correction determined from one mass can be applied to the field values of other calibration masses and new parameters A and B determined and a precise recalibration can be done using only one measurement. This recalibration procedure is quite general and also could be applied to polynomial calibrations.

Experience with Finnigan-MAT 261 instruments shows that field drift of 0.02 to 0.1% in a calibration is typical over a week and over 2.0% in six months. The weekly variations are sufficient to compromise centring on a desired mass but a detailed multi-mass calibration curve is not practical because of the time and different elements required to maintain it. A procedure has been developed that utilizes the advantages of the new algorithm and minimizes the maintenance of an accurate mass-field reference table. Because only two masses are required to define the parameters A and B for the mass calibration curve, the simplified procedure utilizes only two mass-field calibration values and no detailed calibration is required. Although a minimum of two masses is adequate, additional masses can be included in the mass-field reference table to minimize the interpolation for the field of a required mass. The procedure searches the table for the two

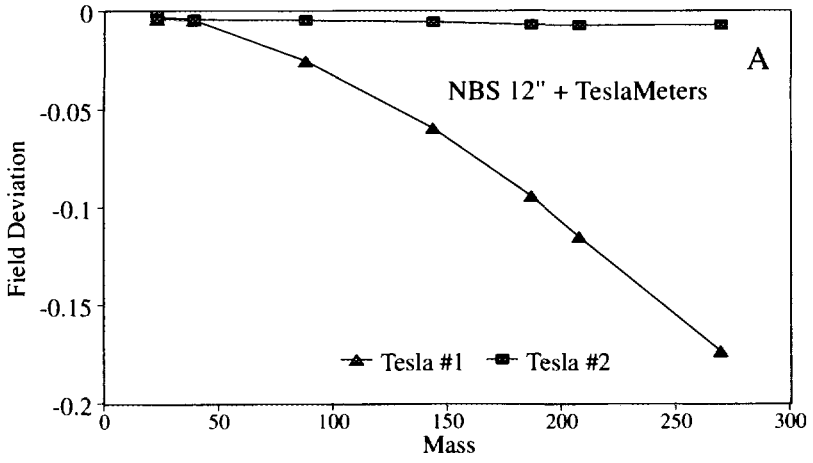

Figure 5A.

Deviations of observed magnetic field intensity at masses 23, 39, 88, 144, 187, 208, and 270 from theoretical values defined by the relation of Equation 2 for a NBS Shields 12" mass spectrometer using two different NIST Teslameters. The field intensity is scaled to the same units and magnitude as the VG 3600 data at a mass of 187. The magnitude and sign of the deviations for Teslameter #1 are similar to the Finnigan-MAT 261 (Fig. 2B) but with greater nonlinearity to the curve.

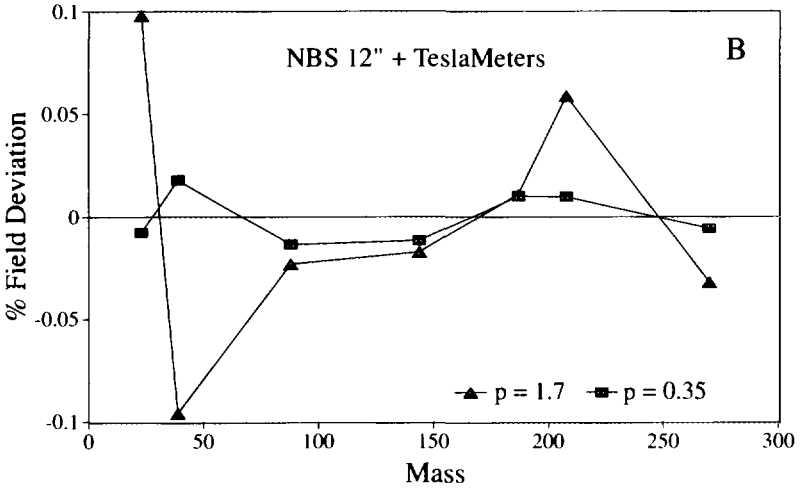

Figure 5B.

A similar plot to Figure 3 for data given in Figure 5A. The deviations are derived from a regression of the field observations using Equation 4. Teslameter #1 has an optimum fit with p = 1.7 and results in parameters of A = 0.32404, B = -0.0000129. Teslameter #2 has an optimum fit with p = 0.35 and results in parameters of A = 0.31410, B = -0.00107, although similarly good fits are attained for p up to 1.0 (excluding p = 0.5).

masses nearest the required mass and uses the associated fields to calculate optimum A and B parameters and then the field of the required mass. Field drift can be corrected in the same manner as outlined above: fractional drift determined from one calibrating mass can be used to correct and update the other calibrated masses in the mass-field reference table.

Routine analyses usually involves measuring intensities of isotopes of a single element (i.e. Pb, Sr, Ar) or a range of elements within a limited mass range (i.e. rare-earth elements). One isotope of an element under analysis is included in the mass-field reference table and the isotopes of interest are analyzed by sequentially focusing ion beams on a detector and repeating the sequence many times. Magnet hysteresis arising from cycling in a limited mass range will result in small divergences from the expected field positions derived from the standard calibration performed over a large mass range. These deviations can be minimized by including another nearby calibrated mass of the same element in the mass-field reference table. The fields of the two reference masses then can be used to determine A and B parameters and thus the field values at other nearby masses in the analysis.

This inclusion of another calibrating mass can be modified slightly to provide additional flexibility. Rather than actually adding an additional nearby or local mass to the mass-field reference table, this mass can be used to establish local A and B parameters which are then retained in a second level calibration. These parameters can then be used to calculate nearby mass positions by difference from a mass in the reference table near the local calibrating mass. The field for this mass is not stored, only the local A and B parameters determined at the time of calibration using the local mass. This local calibration can be optimized to the hysteresis loop actually used during data collection by cycling through the masses to be measured to establish the hysteresis and performing a mass calibration at two calibrating masses (one in the reference table and the local calibrating mass) to establish the local A and B parameters. Other nearby masses in the data sequence then use these local A and B parameters and the field of the nearest mass in the reference table to determine the optimum mass positions. In practise local masses are defined as within ±12 amu of the mass used to establish the local parameters. This technique is particularly useful for establishing precise field positions of a baseline measurement, or a mass with an ion beam intensity which is too small to accurately determine the appropriate field value with a beam centring routine.

There are two reasons for not including the local calibrating mass in the reference table but only retaining the calculated local A and B parameters. First, it is an additional mass to maintain as an up-to-date reference. Second, once established the local calibration parameters A and B are quite

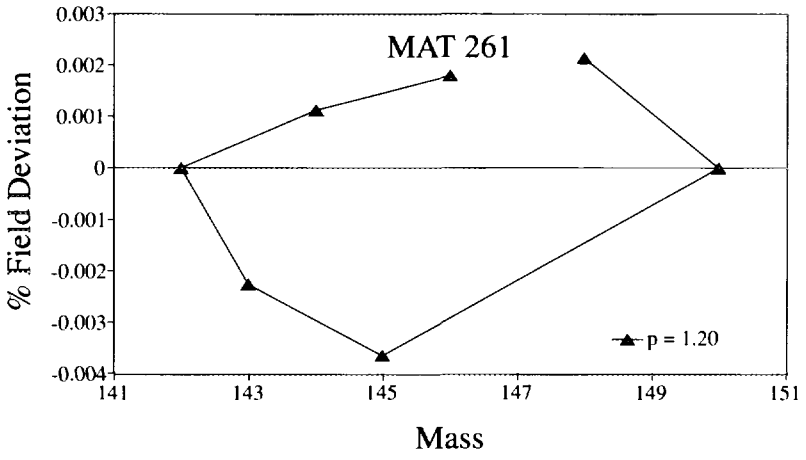

Figure 6.

A plot of deviations of observed magnetic field intensities from calculated values for a Finnigan-MAT 261 in the Nd mass range. The switching sequence loops through masses 146, 144, etc. as shown. The deviations are derived from a two point solution to Equation 3 using observed fields at masses 150 and 142 with p = 1.2 and result in local parameters A = 0.29639, B = -0.000200. Reproducibility of the field values is about ±0.001% using a beam centring routine. This is a different instrument to those used to display results in Figure 4.

insensitive to changes of calibration due to drift. It can be shown (Appendix 1) that the error in field position of an uncalibrated mass, arising from using previously established local A and B parameters, can be expressed as

$$\%\ Field\ Error = (\sqrt{M_2} - \sqrt{M_1})/\sqrt{M_2}\cdot(\%\ drift) \quad (5)$$

where M_1 and M_2 are a currently calibrated mass in the reference table, and the required uncalibrated mass, respectively, and per cent drift is the long term drift in the field since the last local mass calibration. The function strongly demagnifies the field error. For example if the calibrated mass is ^{40}Ar and the field at ^{36}Ar is calculated, the error is 0.051 (% drift) and a 0.1% drift error results in an error in the mass 36 field of 0.005%. At heavier masses the error is smaller and for masses 204 and 208 the error is 0.010 (% drift).

Figure 6 demonstrates the application of this local calibration technique and the levels of error in determining the positions of seven Nd and one Sm isotope analyzed in a Finnigan-MAT 261 instrument. A hysteresis loop was established for the mass sequence 146, 144, 142, 143, 145, 150, 148 and the masses 142 and 150 were used to determine the local A and B parameters. The fields of the other masses, were also precisely determined using a beam centring routine and the plot shows the deviations of the calculated field values from the observed values as a result of using the local calibration parameters to determine their field positions.

DISCUSSION

The algorithm presented as Equation 3 can successfully model the deviation of the mass-field calibration from the theoretical equation (Equation 2) over the mass range of interest for all isotopic analyses. Reasons for deviation from the theoretical relationship can be ascribed to several possibilities. Magnet hysteresis certainly plays a part in some of the small deviations observed and minor magnet saturation could be responsible for the overall divergence from the theoretical value. Saturation could account for the Finnigan-MAT 261 calibrations, however, the VG 3600 calibration shows higher magnet fields at higher masses – the reverse of a saturation effect. Therefore saturation may only be a minor component.

Hall probe linearity is a more likely source of apparent deviation as two different probes (NIST Teslameters) used to control the same NBS 12" mass spectrometer produce different calibrations. In addition, the same Teslameter used on a different Shields NBS mass spectrometer (6") produces a similar calibration to the 12" machine. Calibration for Teslameter #1 is significantly nonlinear and requires a power factor p = 1.7 for optimum fit, whereas the second Teslameter closely approximates the ideal relation (Fig. 5A) and is insensitive to the power factor, with excellent fits for p ranging from 0.35 to 1.0 (excluding the singularity at p = 0.5). This second Teslameter was developed to improve on the first probes characteristics by minimizing the minor intrinsic nonlinearities of Hall probes (R. Schideler, pers. comm., 1994) and clearly measures the magnetic field with greater accuracy and linearity than the first Teslameter. One characteristic of the calibrations of three of the five probe units used is a correlation of significant deviations at the low end of the mass range with greater deviations from the ideal mass spectrometer relation. The VG 3600 shows maximum deviation at masses 2 and 17; a MAT 261 deviates at masses 23 and 39, and the NBS 12" with Teslameter #1 deviates at masses 23 and 39. These calibrations have the largest power factors (p = 1.2, 1.2 and 1.7). In contrast, the better fitting calibrations have more linear deviations (p = 1.0). The two Teslameters on the NBS 12" instrument most clearly demonstrate this correlation and suggest that Hall probes that can accurately and linearly measure magnetic fields will provide the most accurate calibrations of the mass-field relations of magnetic sector mass spectrometers.

Despite the exact source of the deviation from the ideal equation, the algorithm defining the mass-field relation for mass spectrometers controlled with Hall probes appears to have general applicability. In addition to the three types of instruments calibrated here the procedure has also been applied to mass-field data from SHRIMP II, a large radius double focusing ion microprobe (Clement and Compston, 1994). The algorithm is also able to improve on linear and

quadratic calibrations of this instrument. The ability to define an essentially linear relationship results in an efficient technique of calibrating mass spectrometer magnets and maintaining a calibration.

CONCLUSIONS

These calibrations for several different instruments with different electronics for controlling the magnetic field show that the algorithm of Equation 2 has a general application to Hall probe controlled mass spectrometers. There are several advantages of this algorithm over usual polynomial fits:

1. The value of p has a limited range, even for different Hall probe/controllers, and once determined for a probe it can be a fixed value.
2. A fixed p reduces the algorithm to a linear relation with only two unknowns (A, B in Equation 3) and any two widely spaced masses are adequate to define the calibration. This is a significant advantage as a single calibrating standard with two elements of widely differing atomic weight can be used to check and maintain the calibration.
3. Because the mass-field relation has been reduced to a linear relationship extrapolation outside the defined mass range is precise, in contrast to polynomial fits in which extrapolation produces increasing uncertainty in obtaining the desired mass with increasing extrapolation.
4. As the algorithm will yield zero field at zero mass, extrapolation to low masses is similarly precise.
5. The algorithm can be used to assess a calibration because the A and B parameters, once established, have consistent values with little variation. For example, if a recalibration is attempted on the wrong mass (i.e. ^{207}Pb mistaken for ^{206}Pb) the parameters will differ significantly from the expected values and the calibration can be rejected with a warning to the operator.
6. The algorithm can be further refined by the introduction of second level of local calibrating masses to increase the flexibility of the procedure and account for the hysteresis loop. As such, precise field positions for baseline measurement or small mass intensities can be precisely determined.

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REFERENCE

Clement, S.W.J. and Compston, W.
1994: Ion probe parameters for very high resolution without loss of sensitivity; in Abstracts of the Eighth International Conference on Geochronology, Cosmochronology and Isotope Geology, (ed.) M.A. Lanphere, G.B. Dalrymple, and B.D. Turrin; United States Geological Survey Circular 1107, p. 62.

APPENDIX 1

Effects of field drift on use of local parameters

From Equation 3 with

$$p = 1.2: F = A \cdot \sqrt{M} + B \cdot M^{1.2}$$

The field at one mass position can be expressed in terms of the field at another mass and the A and B parameters. The field F_2 at an uncalibrated mass M_2 in terms of the field F_1 at M_1, a calibrated mass is

$$F_2 = F_1 + A \cdot (\sqrt{M_2} - \sqrt{M_1}) + B \cdot (M_2^{1.2} - M_1^{1.2})$$

For analysis in a limited mass range (±12 amu) the A and B parameters can be calibrated locally in this mass range to provide precise field positions. If the field has drifted and a recalibration of the local A and B parameters carried out a new F_2' is

$$F_2' = F_1' + A' \cdot (\sqrt{M_2} - \sqrt{M_1}) + B' \cdot (M_2^{1.2} - M_1^{1.2})$$

Suppose that the field of calibrated mass M_1 is corrected for the drift (to F_1') but the old local A and B parameters are used for calculating the field of M_2, then

$$F_2'' = F_1'' + A \cdot (\sqrt{M_2} - \sqrt{M_1}) + B \cdot (M_2^{1.2} - M_1^{1.2})$$

The error in the field of M_2 because of the use of the old local parameters is therefore:

$$F_{err} = F_2' - F_2'' = (\sqrt{M_2} - \sqrt{M_1}) \cdot (A' - A) + (B' - B) \cdot (M_2^{1.2} - M_1^{1.2})$$

For the calibration data in Table 1 the second term in the above equation is only 1% of the first term in the region of mass 40 and about 3.9% near mass 207, corrections small enough to ignore the last term. This approximation is equivalent to assuming B = 0 and the theoretical relation in Equation 2 applies.

Thus the % error in the field of M_2 can be simplified to

$$\%F_{err} = (\sqrt{M_2} - \sqrt{M_1}) / \sqrt{M_2} \cdot (A' - A) / A \cdot 100$$

Since % drift in field can be approximated by (A' – A)/A·100 then

$$\%F_{err} = (\sqrt{M_2} - \sqrt{M_1}) / \sqrt{M_2} \cdot (\%\ drift)$$

This relation shows that error in the field is demagnified by the mass terms. For example if the correct mass is ^{40}Ar and the field at ^{36}Ar is calculated the error is 0.051 (% drift) and a 0.1% drift in field results in an error in the field of mass 36 of 0.005%. At heavier masses the error is smaller and for masses 204 and 208 the error is reduced to 0.010 (% drift). Therefore errors in field positions resulting from field drift are generally less than 1/20 of the drift for masses greater than 35 when local calibration parameters are used. This demagnification can be demonstrated graphically by considering that drift in the mass-field relation in Figure 1 rotates the calibration curve about the origin. This shifts the field values but the local slope of the line at any point is relatively insensitive to this shift of field and changes by a much smaller amount.

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