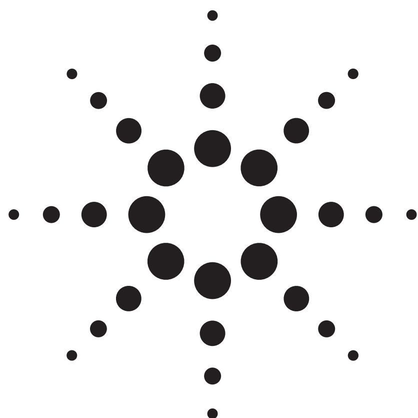

The Determination of Impurities in Nitric Acid and Hydrofluoric Acid by ICP-MS

Application Note

Semiconductor

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John Gomez, and
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Abstract

This application note describes the 4500 ICP-MS analysis of concentrated nitric and hydrofluoric acids used in semiconductor production. PPT level determinations are required for these reagents. Sample preparation was just simple dilution. Low dilution factors were used to analyze the acids thereby minimizing sample contamination and allowing for the best possible detection limits. Ten elements were analyzed. The ShieldTorch and cool plasma conditions made the analysis of K, Ca and Fe possible. All elements were analyzed under the same conditions. Detection limits were in the range of 1 to 30 ppt. MSA calibration curves in this concentration range were linear.

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Introduction

In the semiconductor industry, the presence of metallic contaminants in reagents used in the manufacturing process adversely affects the production yield of semiconductor devices. Moreover, the drive towards sub-micron devices places even greater demands on the manufacturers of acids used in semiconductor production.

Semiconductor acid manufacturers were among the first to recognize the excellent detection power of ICP-MS, and the technique is used widely in the industry. One limitation of quadrupole ICP-MS, however, is the spectroscopic interferences on Fe, K and Ca, which compromise detection limits for these elements which are important to the semiconductor industry. Until recently, the analysis of these elements had been performed concurrently by GFAA. The 4500 ICP-MS employs a patented ShieldTorch interface and cool plasma conditions to enable the determination of these elements at ppt levels, so that all the elements of concern to the semiconductor industry can be measured by the 4500 ICP-MS alone.

Nitric acid and hydrofluoric acid are both widely used in the semiconductor industry. This application note describes how the 4500 ICP-MS is used to quantitate all the metallic impurities required to be measured by the semiconductor industry at the ppt level by simple dilution and direct analysis.

Instrumentation

A standard 4500 ICP-MS is equipped with the inert sample introduction kit. This kit is comprised of a polypropylene spray chamber and solid platinum torch injector for best resistance to aggressive reagents while ensuring negligible sample contamination. The 4500 ICP-MS was also fitted with the optional microconcentric nebulizer (MCN), which gives the same sensitivity as conventional pneumatic nebulizers, but at a much lower sample uptake rate (~20 µL/min.). This sample introduction configuration could also be used for the analysis of microvolume samples such as those resulting from the vapor phase decomposition (VPD) of Si wafers.

Sample preparation

The excellent detection limits of the 4500 ICP-MS mean that low ppt levels can be determined without the need for sample evaporation and preconcentration. This analysis was performed by simply diluting the acids prior to measurement. Nitric acid (60%) was diluted 2+1 and hydrofluoric acid (40%) was diluted 3+1 with ultrapure water (Milli-Q SP: Nihon Millipore Ltd.).

Operating conditions

All data were obtained in a single run. The ShieldTorch system combined with cool plasma conditions was used for the analysis of all elements. The ShieldTorch system significantly reduces isobaric and polyatomic interferences that affect the low level determination of ^{39}K (^{38}ArH), ^{40}Ca (^{40}Ar) and ^{56}Fe (^{40}ArO) (*1*).

Instrument Conditions

RF power:	900 W
Sampling depth:	13 mm
Plasma gas:	16 L/min
Auxiliary gas:	1.0 L/min
Carrier gas:	1.8 L/min
Nebulizer:	MCN

Data acquisition parameters

Points/peak:	3
Integration time/mass:	3sec
Repetitions:	10

The Influence of Metallic Impurities on Device Performance

In this study, 10 elements (Na, Mg, Al, K, Ca, Cr, Fe, Ni, Cu and Pb) which are of key importance in the semiconductor industry were measured. The presence of alkali metals such as Na and K can cause shifts in threshold voltage. They can also influence minority carrier lifetime, and their presence can result in increased leakage current and reduced oxide breakdown voltage. Heavy metals such as Cu and Fe lower the minority carrier lifetime while increasing dark current and leakage current and give rise to greater epi structural defects. Ni and Cr also generally cause a reduction in minority carrier lifetime and oxide breakdown voltage, and tend to increase structural defects in epi films (*2*).

Analyses were performed using the method of standard additions (MSA) on each sample. For the determination of each unknown sample, five solutions were measured - the unspiked sample and four spiked aliquots. The added spike concentrations in solution were 50, 100, 150 and

Element	m/z	Measured	DL
Na	23	110	5
Mg	24	20	1
Al	27	40	3
K	39	450	10
Ca	40	450	10
Cr	52	8	1
Fe	56	150	30
Ni	60	33	7
Cu	65	180	20
Pb	208	9	5

Units: ng/L (ppt)

Table 1
Quantitative results for 40% HNO_3

Element	m/z	Measured	DL
Na	23	100	7
Mg	24	5.2	0.8
Al	27	37	9
K	39	170	7
Ca	40	380	20
Cr	52	10	2
Fe	56	53	7
Ni	60	30	4
Cu	65	70	8
Pb	208	6.2	0.7

Units: ng/L (ppt)

Table 1
Quantitative results for 30% HF

200 ng/L (ppt). Data were plotted as a five point calibration curve using a least squares fit. The concentration of each analyte in the original sample was calculated from its respective standard addition calibration curve.

Results

Appendixes 1 and 2 show the calibration curves of nitric acid and hydrofluoric acid obtained by MSA. In general, excellent correlation coefficients were obtained considering the concentration levels involved. The concentration of each element in the sample is shown underneath the corresponding calibration curve. Clearly, from the good fit of the 50 ppt point on each calibration curve, less than 50 ng/L (ppt) of analyte can be reliably quantitated.

Tables 1 and 2 show the quantitative results and the detection limits (DL) of the analytes for each acid obtained in this study. DLs were calculated using three times the standard deviation of ten measurements of the unspiked sample divided by the slope of the MSA curve. The integration time for each element in this analysis was set to three seconds, and the detection limits obtained were extremely good - in the range of 1 to 30 ng/L (ppt) for 40% nitric acid and 0.7 to 20 ng/L (ppt) for 30% hydrofluoric acid. However, detection limits are affected by the concentration of the analyte in the acid.

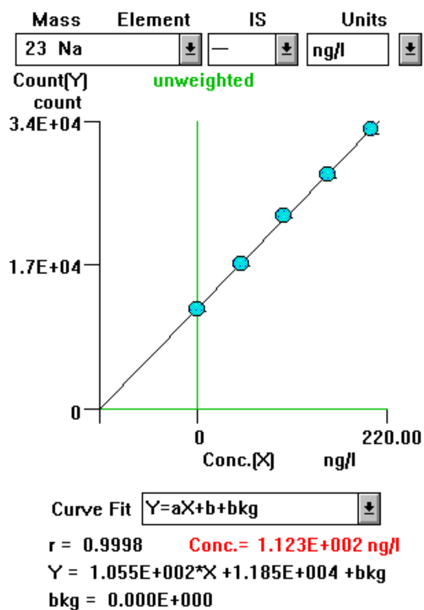
These low detection limits were achieved due to some unique design features found in the 4500 ICP-MS. The ion lens train features an omega lens which bends the ion beam into an off-axis quadrupole, rather than defocusing the ions around a conventional photon stop. This results in higher ion transmission across the mass range, and since photons are more effectively prevented from reaching the detector, this also gives the lowest random background in quadrupole ICP-MS - typically <2 cps.

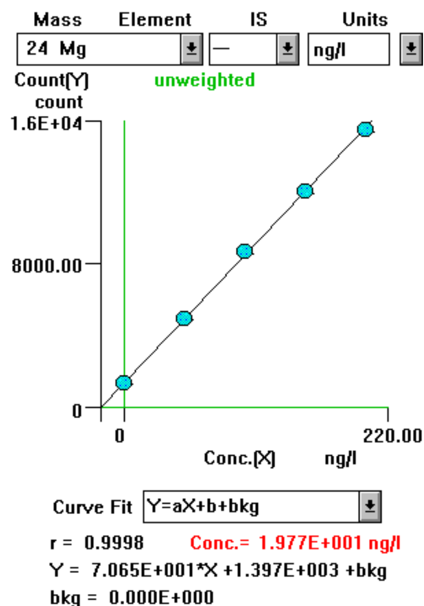
Finally, since the 4500 ICP-MS inert sample introduction kit uses a solid Pt torch injector instead of the conventional alumina or sapphire injector, the detection limit obtained for Al was very low - even in 30% hydrofluoric acid.

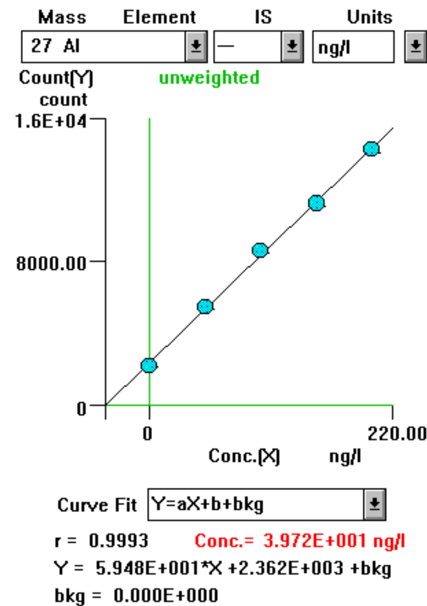
Conclusions

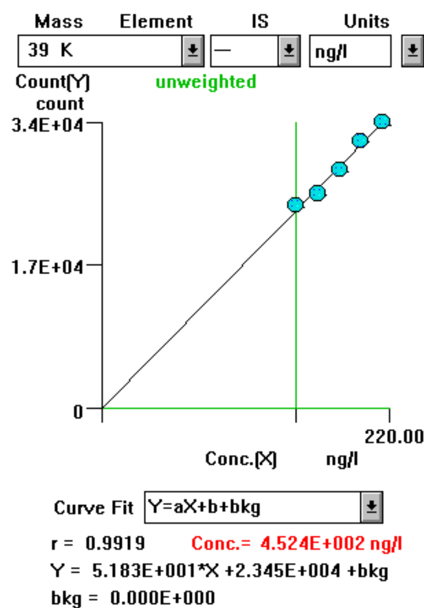
Using the 4500 ICP-MS with the ShieldTorch system and MCN, low ppt level determination of impurities in high concentrations of nitric acid and hydrofluoric acid is possible. The ability to analyze samples directly at low dilution factors nor any preconcentration saves time and reduces the risk of sample contamination.

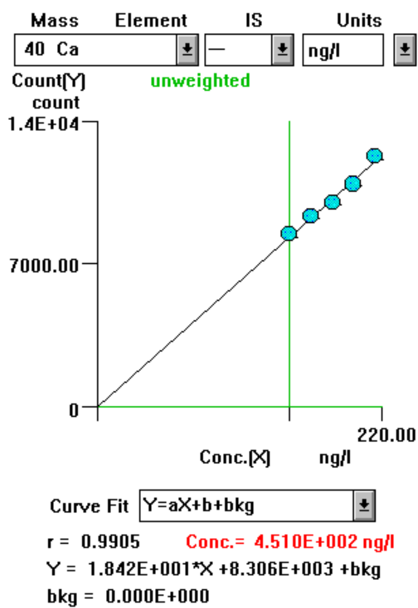
The ShieldTorch enables the low ppt level determination of K, Ca and Fe by reducing the spectral interferences that normally affect those elements. Detection limits of most elements are in the low ppt range and all are analyzed under the same instrument conditions.

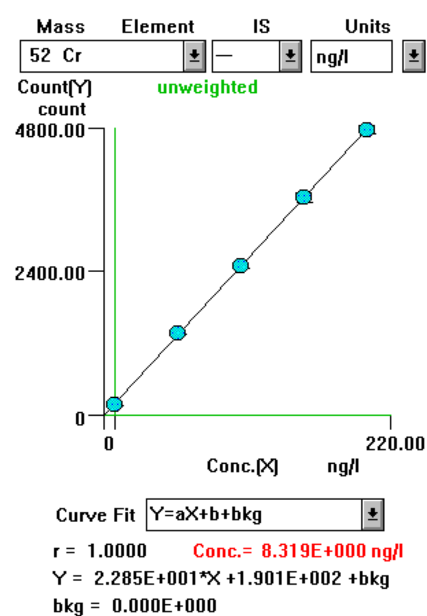




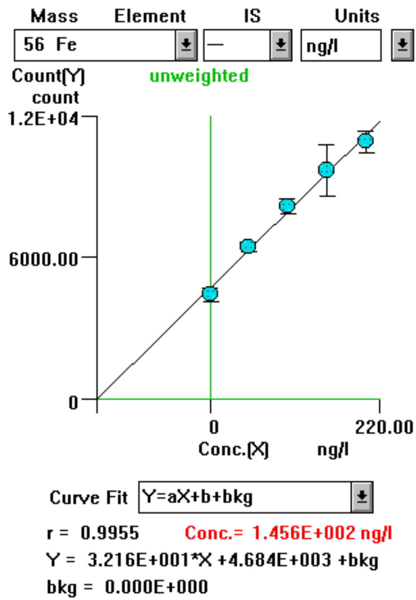


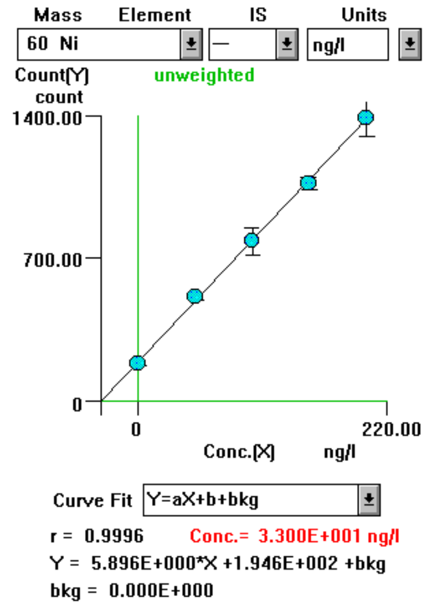


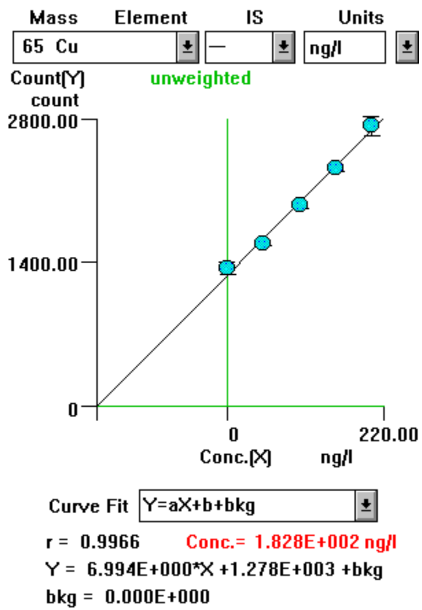


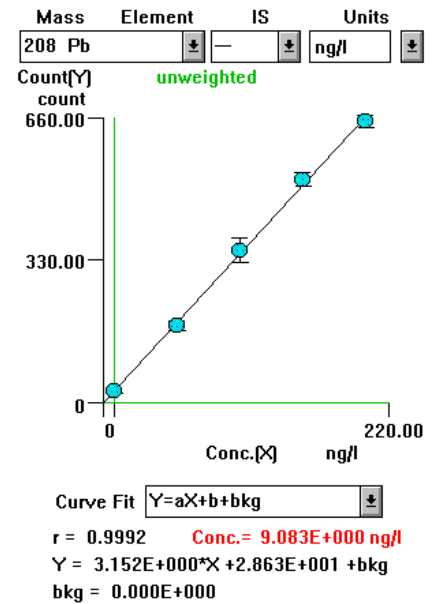


Appendix 1-1 Calibration Curves for 40% (v/v) HNO_3



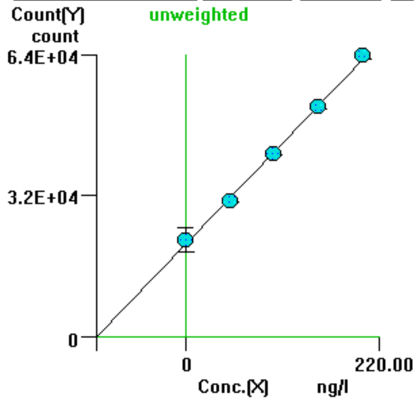






Appendix 1-2 Calibration Curves for 40% (v/v) HNO_3

Mass | Element | IS | Units
23 Na | — | ng/l



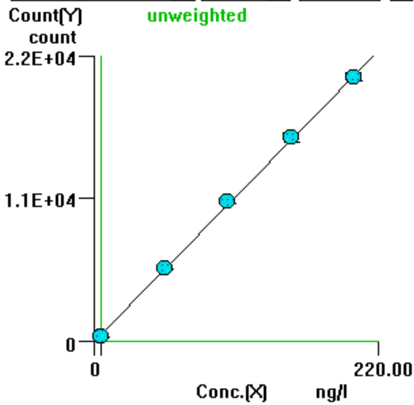
Curve Fit Y=aX+b+bkg

r = 0.9989 Conc.= 1.000E+002 ng/l

Y = 2.092E+002*X +2.092E+004 +bkg

bkg = 0.000E+000

Mass | Element | IS | Units
24 Mg | — | ng/l



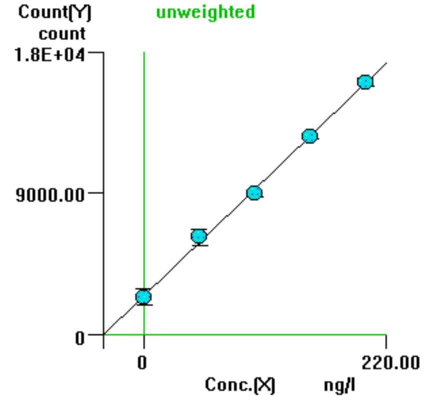
Curve Fit Y=aX+b+bkg

r = 0.9997 Conc.= 5.169E+000 ng/l

Y = 9.989E+001*X +5.163E+002 +bkg

bkg = 0.000E+000

Mass | Element | IS | Units
27 Al | — | ng/l



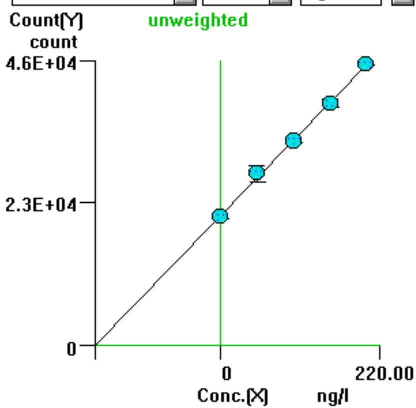
Curve Fit Y=aX+b+bkg

r = 0.9991 Conc.= 3.710E+001 ng/l

Y = 6.724E+001*X +2.495E+003 +bkg

bkg = 0.000E+000

Mass | Element | IS | Units
39 K | — | ng/l



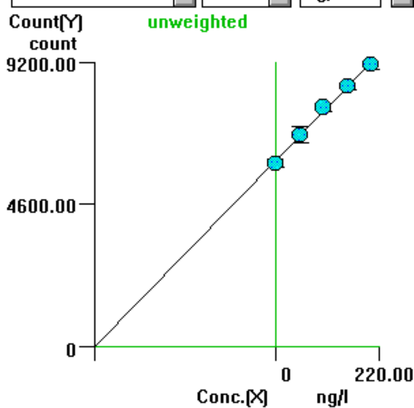
Curve Fit Y=aX+b+bkg

r = 0.9992 Conc.= 1.728E+002 ng/l

Y = 1.212E+002*X +2.094E+004 +bkg

bkg = 0.000E+000

Mass | Element | IS | Units
40 Ca | — | ng/l



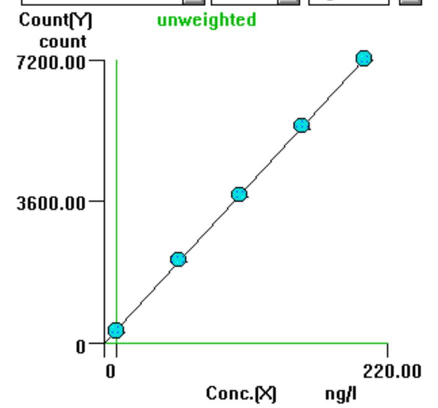
Curve Fit Y=aX+b+bkg

r = 0.9972 Conc.= 3.809E+002 ng/l

Y = 1.575E+001*X +5.999E+003 +bkg

bkg = 0.000E+000

Mass | Element | IS | Units
52 Cr | — | ng/l



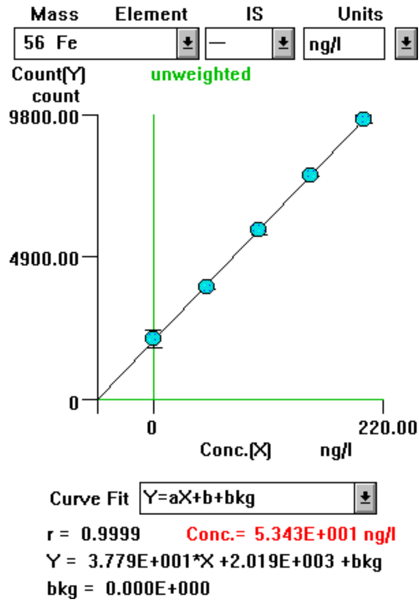
Curve Fit Y=aX+b+bkg

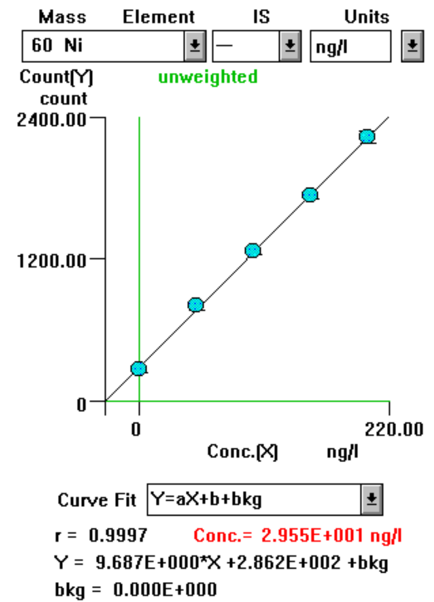
r = 0.9999 Conc.= 9.840E+000 ng/l

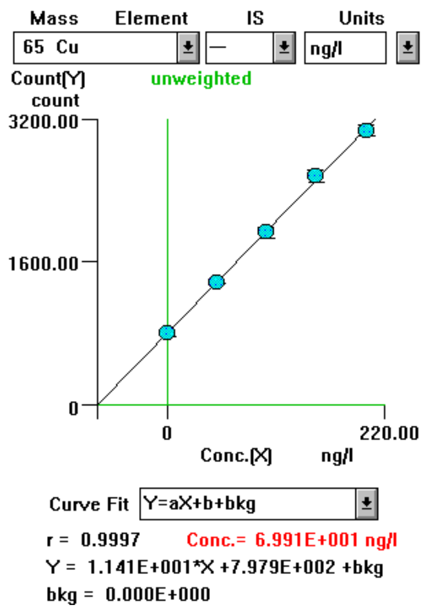
Y = 3.433E+001*X +3.378E+002 +bkg

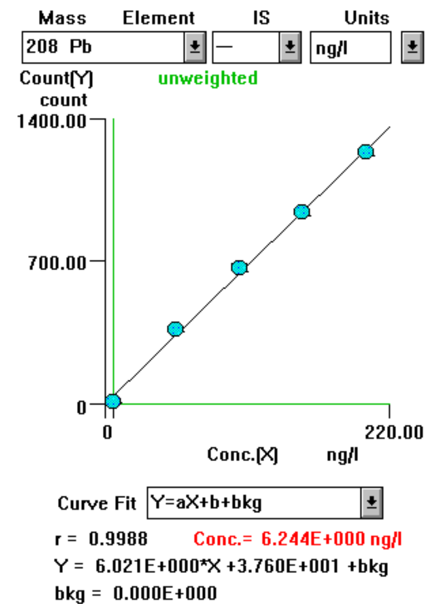
bkg = 0.000E+000

Appendix 2-1 Calibration Curves for 30% (v/v) HF









Appendix 2-2 Calibration Curves for 30% (v/v) HF

References

(1) K. Sakata, K. Kawabata, *Spectrochimica Acta* Vol. 49B No. 10, 1027 (1994)

(2) D. C. Burkman, C. A. Peterson, L. A. Zazzera and R. J. Kopp, *Microcontamination*, November, 57 (1988)

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