OPERATION OF
INDUCTIVELY COUPLED PLASMA SOURCE
MASS SPECTROMETERS
IN THE
PEAK-JUMPING MODE

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ABSTRACT

Operating any spectrometer in a peak-jumping rather than scanning mode improves the fraction of data collection time spent monitoring peaks of interest. This results in improved sensitivity. Several problems with the use of peak jumping with the VG Elemental Plasmaquad inductively coupled plasma source mass spectrometer (ICP-MS) are discussed. Software and hardware changes installed to overcome these limitations are presented. Of particular importance, is the identification of limitations on peak-jumping speed and the need for built in delays (>0.5 msec) to allow for the response time of the quadrupole's electronics.

INTRODUCTION

The sensitivity of a spectrometer for any particular species is limited by the fraction of data acquisition time which is spent monitoring the signal generated by that species. Ideally, one would monitor all signals simultaneously thereby not only collecting the maximum signal but also avoiding biases caused by drifts in instrumental response with time.

With a quadrupole mass filter such as that used in inductively coupled plasma source mass spectrometers, simultaneous collection is not possible. Two alternative modes of data collection can be used. Each has advantages and disadvantages. In the scanning mode, a region of the spectrum is swept at a uniform rate. The width of the region and the speed of sweeping (scanning) are at the discretion of the operator. Typically many sweeps are made and summed into a single spectrum. This is done to average out noise and drift which might bias a spectrum scanned only once. The advantages of operating in the scanning mode are that data are collected for all masses in the region of interest and simplicity of setup. The principal disadvantage is that equal time is spent on all peaks. On the other hand, in peak jumping, one only samples selected points (peak tops) within the spectrum. The advantages of peak jumping are being able to spend a larger fraction of the collection time on minor peaks - thereby improving the precision of their determination, to sample only peak tops further improving precision, and to skip unwanted or excessively intense peaks. The disadvantages of peak jumping are the necessity of accurately sampling the proper portion of each peak and the possible loss of interesting data by making a poor choice of masses to sample.

In addition to the extremes of continuous scanning and peak jumping, intermediate data collection scenarios are possible and often employed. For example in skip-scanning, selected mass regions can be skipped; i.e., scanned very rapidly. This avoids lingering on high intensity peaks which could damage the ion detector and allows one to sample several regions of interest while not spending appreciable time on connecting regions.

When peak jumping, one would like to have flat-topped peaks so that instabilities in the instrument would not cause the signal to drift out of the detector. This situation is illustrated by low resolution magnetic sector mass spectrometers in which the collector slit is significantly wider than the spread of the ion beam. Moderate variations in ion energy or magnetic field do not cause part of the beam to be excluded from the detector. In quadrupole systems, peaks are typically triangular in shape. It is therefore difficult to be sure one is reproducibly sampling the top of each peak. Even if the electronics were of sufficient stability to allow such sampling, the peak shapes are typically somewhat "ragged" making it difficult to determine where the true top is. For these reasons, it is desirable to be able to sample several points over the top of each peak.

The choice of a data collection scheme is then in all cases a

compromise and the distinction between scanning and peak jumping blurs with the possibilities of hybrid techniques. The purpose of this report is to evaluate the peak-jumping mode and selected variants with respect to the improvements and limitations they provide. While many of the principals discussed will apply to any quadrupole based ICP-MS, specifics will apply to the VG Elemental Plasmaquad. This instrument is in use at several Department of Energy laboratories including Lawrence Livermore National Laboratory, Los Alamos National Laboratory, Savannah River Laboratory, and Pacific Northwest Laboratory.

HISTORICAL PERSPECTIVE

As originally conceived the Plasmaquad was a scanning instrument, but even the earliest production units included provisions for skip-scanning to protect the detector from exposure to the high intensity water and argon peaks. The skip-scanning option was also useful for omitting undesired regions from the spectrum thereby spending a larger time fraction collecting data in the regions of interest.

Before going more deeply into the various options, it is necessary to explain a few details of the data collection process and data storage. When the spectrum is scanned, data are stored in a multichannel analyzer operated in the multiscaling mode. Each channel of the analyzer sums the ions detected within a fixed time interval during the mass scan. By synchronizing the sweeping of the quadrupole and the analyzer, a spectrum is obtained in which each point is the sum of the ions observed in a given mass region. Repetitive scans are summed to give the final spectrum (Fig. 1). The number of analyzer channels used to collect a spectrum can be varied in powers of two between 512 and 4096. The choice of the number of channels and the width of the mass region to be scanned partially determine the precision and resolution with which a peak can be measured. In that peak areas are used to calculate isotopic ratios and concentrations, the selection of the number of channels per mass unit is important. For concentration measurements, the use of ≈ 10 channels per mass unit is sufficient whereas for isotopic ratio determinations ≈ 50 channels per mass is desirable. A limitation to the skip scan approach for separated mass regions was that analyzer channels were reserved for the skipped masses as well as those actually scanned. This limited the number of channels per mass unit which could be used.

It was quickly realized that peak jumping would be desirable. Early versions offered by VG had severe firmware and software limitations. These will not be discussed in detail. Suffice it to say that partially at the suggestion of the authors, VG developed a system which allowed the operator to select the number of points to be sampled over each peak, how these points were to be spaced, what masses would be sampled, and what fraction of the acquisition time would be spent on each peak (Fig. 2). In practice an actual dwell time per point is selected rather than a fraction of the time. This dwell time determines how rapidly a single pass through the mass region is to occur. As in the scanning case, multiple passes are summed in the analyzer to give the final spectrum. This "second

generation" VG package was the starting point for the work presented here.

The details of the construction of the multichannel analyzer and the firmware which controls it impose constraints on the data collection options that can be used on a given Plasmaquad. We must therefore review this history. In the early instruments VG used an analyzer manufactured by Tracor Northern. The signal processing time of this unit (≈ 50 nsec) controlled the overall "dead time" of the system and thereby limited the maximum signal which could be counted. (The detection system is operated in the pulse counting mode.) The firmware supplied with this analyzer did not support peak jumping except as a series of skip scan regions. It was also not possible to set different dwell times for different masses. We made various attempts to overcome these limitations but were fundamentally limited by the firmware which we had no ability to modify. At the time we were discussing the need for a peak-jumping scenario of the type described above, VG was developing their own (faster) multichannel analyzer and new firmware to support it. It was their decision to incorporate ideas similar to ours in the new firmware but not to rewrite the firmware supporting the Tracor. At this point, we upgraded to the VG analyzer and continued our development work using that system.

SYSTEM REQUIREMENTS

Because the hardware, firmware, and software of the Plasmaquad have each gone through several versions, it is difficult to list the combinations of modifications which would be required to use the various features to be described. It is our opinion that instruments currently equipped with the Tracor analyzer should be upgraded to the VG analyzer. Any issue of the firmware used by the microcomputer in the Plasmaquad should be acceptable if it supports the VG analyzer. We operate our instruments on a highly modified version of the VG Issue 2.01 software. This software can be made available to other laboratories. In addition to the peak-jumping features to be described, it incorporates a number of other changes which we have found useful. There are certain limitations to its use. We have of necessity changed the format of certain files including data files. Being a modification of Issue 2, it uses the Sigma Dazzler card to drive the display. Issue 3 uses the enhanced graphics adapter (EGA) standard in place of the Dazzler. For this reason, Issue 3 users who do not have access to a Dazzler card can not run our software unmodified. Unfortunately the Dazzler card is no longer in production, and to our knowledge, there is no substitute. The techniques discussed here are applicable to other software versions but recoding would be required.

SOFTWARE IMPROVEMENTS

In the VG peak-jumping software, the counts for the data points measured for each mass were summed to give a single number for each isotope. The raw data; i.e., the channel by channel data were not stored. This approach has two deficiencies. First, by not saving the data as collected, it was impossible to identify problems with peak

centering or drifts in the mass calibration. Secondly, in summing the various points measured over a peak, it is necessary to correct the observed counts for dead time losses. This correction depends on the count rate in the individual channels. If an incorrect dead time were used, it would be impossible to redo the calculation without the raw data. For this reason, we added a routine to save the raw data.

Because of the possibility of shifts in mass calibration during a series of data acquisitions, we included an option for recalibrating existing data. For spectra collected in the scanning mode, data exist for the entire mass region. It is therefore straightforward to calibrate the mass scale. One identifies the mass of two or more peaks and fits a linear mass scale to the channel numbers.

The situation is somewhat more complicated for peak jumping because data are not available for a continuous mass region. One only has data for a set number of channels spaced over a fixed fraction of a mass unit around each selected mass. Typically improper calibration will result in sampling the same portion of all peaks, but the channels will not be centered on the peak. This is not a problem if the mass resolution is high and only the center portion of the peaks is being sampled. In cases where most of the peak width is being sampled, recalibration is accomplished by redefining the peak centers and including fewer channels in the peak integrals.

To support these changes in the software, it was necessary to modify the structure of the data files. In addition to storing additional "header" information describing the parameters of the acquisition, dwell time data had to be stored for each mass. This information is stored in both the "raw" and "integrated" data files (Appendix 1).

As implied above, the accurate measurement of peak areas and hence isotopic ratios requires that the same relative portion of each peak be measured. In the VG software, the instrumental setting corresponding to transmitting the center (most intense signal) of each peak is determined by analyzing a solution containing all of the peaks of interest. For certain masses, this approach can not be used either because a suitable "marker" isotope is not available or its use would contaminate the instrument. For example, in the analysis of uranium isotopic ratios, ^{236}U does not exist in nature and ^{234}U occurs at a very low level, 55 ppm. While both of these isotopes can be obtained at high enough levels to use in mass calibration, their use would provide a significant source of chemical blank, and should be avoided. An even greater problem is presented by the need to determine the instrumental background count rate. This is best done by measuring the count rate at a mass where no peak is present. In the uranium example, mass 240 is a good choice. In this case, there is no isotope which can be used to determine the center of the peak unless one is willing and permitted to handle plutonium.

These limitations lead us to develop a different peak-centering routine based in part on our experience with magnetic sector peak jumping. In our routine, first a spectrum is collected using the peak-jumping procedure to be used in the analysis and a default mass calibration. For each mass if the number of counts exceeds a

preselected threshold, a running sum of three channels is constructed and the peak center defined as the middle channel of the highest sum. If the observed counts of two or more peaks exceed the threshold, a mass calibration is fit to those peaks and applied to the masses with intensities below the threshold (Fig. 3). If only one peak exceeds threshold, the default calibration is linearly shifted to match that peak. If no peak exceeds threshold, the default calibration is maintained. A typical threshold would be 10,000 counts. The operator has the opportunity to repeat the calibration as many times as desired to test for stability or to bring the peaks into calibration if the default settings were sufficiently "off" to cause the initial trial to miss the peak tops. Normally recalibration is not necessary. After calibration is complete, samples are analyzed. Because the raw data for each accumulation are displayed at the end of acquisition, it is possible to monitor for any drifts/shifts in calibration. If such shifts occur, the operator has the option of recalibrating between samples.

A LIMITATION

As a first evaluation of the capability of peak jumping as compared to scanning, isotope ratios in a lead standard (National Bureau of Standards SRM 981) were measured using conditions similar to those which had given the best results in the scanning mode. The same number of points per peak, 39, and the same fraction of the peak width as included in the integration of the scanned peaks were used. The same dwell time, 80 μ sec, was used for the major isotopes - 206, 207, and 208. The dwell time for mass 204 was increased to 640 μ sec. In the scanning case, a ten mass unit range was sampled. By collecting data on only the four lead peaks and only 90% of the width of each, the actual data collection time was approximately the same for the two modes. The principal difference was spending a much larger fraction of the available time on 204 while not reducing the time spent on the other lead isotopes. The 208/206 ratio was used to correct the 207/206 and 204/206 ratios for mass bias in the spectrometer. The results for 207/206 were in good agreement with the NBS values but the 204/206 values were consistently low by $\approx 15\%$ (Fig. 4).

To better characterize this effect, a series of tests was undertaken. To improve the precision of the tests, only the major lead isotopes were measured. The dwell times for 206 and 208 were kept equal to each other and varied relative to the 207 dwell. As shown in Figure 5, when the number of points per peak was reduced from 39 to 9 thereby sampling a smaller fraction of the peak width, the discrepancy was reduced from 16% to 5%. When the 207 dwell was set to a fixed, long time (>20 msec) and the 206, 208 dwell time varied, the discrepancy decreased as dwell time was increased.

Because the error was in the direction of too many counts for the peaks with the shortest dwell times, we thought there might be an error in the timing circuits or the software which added a constant excess counting time to each point. This was demonstrated not to be the case. By setting the quadrupole to transmit a fixed mass and disabling the quadrupole sweeping circuit, all aspects of the system

except the quadrupole were tested. The observed counts were in precisely the ratio of the selected dwell times. This eliminated the counting circuits, timing circuits, and software as potential sources of the problem and left only the quadrupole. In retrospect perhaps this should not have been a surprise because it was recognized early on by VG that the observed mass calibration of a Plasmaquad operated in the scan mode depended on the scan speed. This effect is usually attributed to the voltages driving the quadrupole lagging behind the computer commanded values at high scan rates. In peak jumping, a different but related problem appears to occur. When the computer instructs the quadrupole settings to increment to the next mass value, the direct-current (DC) and radio-frequency (RF) voltages which drive the quadrupole are stepped. Because of the resistive-capacitive (RC) time constant of the voltages, there is a delay between the command to increment and the actual appearance of the correct voltages. This delay is much greater for the DC than RF voltage. In effect for a time the RF voltage has been changed without a corresponding change in the DC. When this happens, the transmission of the quadrupole is increased and the resolution decreased (Fig. 6). For short dwell times, this period of increased transmission is more significant than for long dwell times due to decreased resolution occurring for a higher percentage of the time. The effect is also more severe on the sides of peaks than near the top because of the change in resolution, and the effect is more severe in cases where a large fraction of a mass unit is included in the area sampled. While this has not been proven to be the cause of the observed effect, it is entirely consistent with the observations.

The possibility of such an effect occurring for large mass jumps was anticipated by VG and they included a delay at the beginning of each mass. For peak jumping, we have typically set this value to 1 msec. For large changes in mass between successively measured peaks, a longer delay may be required. (For scanning, 10 msec is typically used because of the large change in voltages associated with switching from the end of a scan back to the beginning.) Between points within a single mass, the only delay was $\approx 3 \mu\text{sec}$ during which the acquisition was gated off while the analyzer changed channels. No provision was made for a longer or selectable delay. For the case in which the acquisition points are 0.02 masses apart, the fractional voltage change per point in the lead region (mass 200) is only one part in 10,000. One might not expect a significant lag for such a small change. The measured deviations (Fig. 5) show that the change in transmission is sufficiently important to effect measurements lasting for a millisecond. It could be either very large for a short duration implying the voltages tend toward zero during the switching interval or small but long lasting. The fact that long dwell-time peaks do not show the effect does not mean that the problem goes away under those conditions, but that it is masked by occurring over a small fraction of the total time.

To demonstrate that the effect was not instrument specific, measurements were made using two other Plasmaquads. One was a relatively old unit with a slightly different configuration of components in the RF power supply of the Model 12-12 quadrupole. The other was a PQ2 equipped with the more modern SX300 quadrupole. Both

instruments showed similar effects to those reported here. In the case of the SX300 quadrupole, the errors in the lead ratios were roughly half as large as with the older units, but in all cases they were significant. We conclude that this imposes a fundamental limitation on the way in which peak jumping can be used. This point will be discussed further below.

Because the effect was controlled by both the dwell time and spread of measured points across the peak, it was judged impractical to develop an algorithm to correct the measured data. A hardware "fix" was therefore required. The obvious modification was to delay the start of data acquisition for each channel by a switch selectable time interval. This was found to be impractical because the corresponding delay in the end of acquisition caused the system to "hang". The solution finally employed was to delay the start of acquisition but not the end. The actual acquisition time was therefore reduced by the amount of the delay (Fig. 7). The software was correspondingly modified to correct the nominal dwell time to the actual dwell time. Figure 8 is the schematic of the modification made to the electronics. The delay is set by switches internal to the chassis. A switch on the front panel activates the circuit for peak jumping. For scanning, the delay is deactivated because all channels have the same dwell time in scanning. Consequently the lag of the quadrupole is equal at every point in the spectrum and does not effect peak ratios. In practice the delay needed for peak jumping is long compared to the 80 μ sec dwell time we typically use in scanning.

Figure 9 summarizes the results for lead isotopic ratios measured with different delays. The results for no delay are those previously shown (Fig. 5). With a 200 μ sec delay, the ratios are appreciably in error for dwell times as long as 1.28 msec. Even with a 500 μ sec delay dwell times of >1 msec are required to obtain ratios which are not obviously biased. Note that with a 1 msec dwell and 500 μ sec delay, half of the total sampling time is wasted.

RECOMMENDATIONS

The appropriate use of the peak-jumping mode of data collection can yield higher precision measurements of minor isotopes than can be obtained using scanning (Fig. 10). The response time of the quadrupole precludes sweeping the region as rapidly as has been found to be advantageous in scanning. Measuring ≈ 9 points spaced over ≈ 0.2 amu for each mass allows one to be sure the same fraction of each peak is measured without significantly reducing the count rate by making measurements on the sides of peaks. Restricting measurements to near the peak tops also minifies the error introduced by the response time of the quadrupole. A delay of ≥ 500 μ sec before the start of data acquisition is necessary for each point to allow the quadrupole voltages to approach their equilibrium values. This limits the dwell time per point to ≥ 1 msec to avoid expending more than half the total data acquisition cycle and hence sample while not collecting data. Dwell times of ≥ 5 msec per point are necessary for the shortest dwell peaks to keep the unused time below 10%. This means that dwell times of ≈ 50 msec are needed for minor

peaks. For the lead case, where one might want to measure 202 for possible mercury interference, 204, 206, 207, 208, and 210 as a background, the ratio of dwell times might be 2/8/1/1/1/2 so that roughly half of the acquisition time is spent on the minor 204 peak. If nine points are measured for each peak, the minimum dwell time is 5 msec, and a 1 msec wait is used before each mass, then the time require to complete one pass through the masses is ≈ 0.7 sec. This is reasonable. On the other hand, if many peaks were to be measured, this time could rise to $\gg 1$ sec. In such a case, the degradation of precision due to sensitivity drifts might exceed the gain in precision sought by peak jumping. It would be unwise to set strict rules for deciding the collection scheme to be used. It is better to evaluate each situation in terms of the considerations presented.

APPENDIX 1

Both raw and integrated data are stored in binary files. In each case, header information describing the conditions used in collecting and analyzing the data is collected in a "block". This header block has the same form for both types of files. The header is followed by the data block. The contents of the data block depend on the file type. Additional information such as the mass numbers for integrated files and peak-jumping parameters are stored in additional blocks. The following two pages are a print out of the file which defines the structure of the data files. Portions which we have changed are indicated by filled circles in the margin. Not all of the changes indicated involve peak jumping.

DEFINITION MODULE DataStruct;

(*

```
-----
ORIGINATORS : PlasmaQuad Software Group
ISSUE 2.00
Copyright VG Isotopes Ltd / PlasmaQuad
Winsford , Cheshire , ENGLAND
-----
```

LAST EDIT : 02-06-86

*)

FROM ConfigStruct IMPORT ShortFileName, MassCalType;

EXPORT QUALIFIED DataHeaderPT, DataHeaderRCD,
RawDataBlock, RawDataBlockPT, MCADData,
IntDataBlockPT, IntDataBlock,
RealDataRCD, RealDataPT,
PJInfoBlockPT, PJInfoBlock;

TYPE

(* Header block for both raw and integrated data files giving
information of the scan parameters etc. *)

PJInfoBlockPT = POINTER TO PJInfoBlock;
DataHeaderPT = POINTER TO DataHeaderRCD;

DataHeaderRCD =
RECORD

SampDiscript	: ShortFileName;
RunNumber	: CARDINAL;
MassCal	: MassCalType;
StartMass	: REAL;
EndMass	: REAL;
NumOfBytesPerChannel	: CARDINAL;
NumberOfChannels	: CARDINAL; (* Points Per Peak in Peak Jumping *)
NumberROI	: CARDINAL;
StartDac	: CARDINAL;
EndDac	: CARDINAL;
NumberSkippedRegions	: CARDINAL;
SkippedDacValues	: ARRAY [1..36] OF CARDINAL;
DacStep	: CARDINAL;
DwellTime	: REAL;
DeadTime	: REAL;
ConstantArea	: BOOLEAN;
MassPortion	: REAL;
NumberOfSweeps	: CARDINAL;
InternalStdUsed	: BOOLEAN;
InternalStdMasses	: ARRAY[0..9] OF CARDINAL;
Date	: ARRAY [0..20] OF CHAR;
Time	: ARRAY [0..20] OF CHAR;
PeakJump	: BOOLEAN;
FirstPJDataPtr	: PJInfoBlockPT;
NumberOfPJPeaks	: CARDINAL;
SpareReal	: REAL;

```

PJPointsPerPk      : CARDINAL;
Rate               : BOOLEAN
END;

```

(*Raw data record consisting of a header block and an array containing the data collected from the MCA. *)

```
RawDataBlockPT = POINTER TO RawDataBlock;
```

```
MCADData = ARRAY [0..12287] OF CHAR;
```

```
RawDataBlock =
RECORD
  DataHeaderBlock : DataHeaderRCD;
  Block           : MCADData
END;
```

(*Integrated data record consisting of a header block, an array containing the data for integral masses and a linked list of records containing the data for non-integral masses.*)

```
IntDataBlockPT = POINTER TO IntDataBlock;
```

```
RealDataPT = POINTER TO RealDataRCD;
```

```
FullIntData = ARRAY [1..255] OF REAL ;
```

```
RealDataRCD =
RECORD
  Mass      : REAL;
  Counts    : REAL;
  NextDataPtr : RealDataPT
END;
```

```
IntDataBlock =
RECORD
  DataHeaderBlock : DataHeaderRCD;
  Block           : FullIntData;
  NumRealMasses   : CARDINAL;
  FirstRealMassPtr : RealDataPT
END;
```

```

PJInfoBlock =
RECORD
  Mass      : REAL;
  Dwell     : REAL;
  CenterDac : CARDINAL;
  NextPk    : PJInfoBlockPT
END;

```

END DataStruct.

FIGURE CAPTIONS

Figure 1

(a) Spectrum of the mass region including lead collected in the scanning mode. 512 channels were used.

(b) Expanded view of a portion of the spectrum shown in (a). The data for the individual multichannel analyzer channels are shown as vertical bars.

Figure 2

Peak-jumping spectra of the lead region. Data have been collected for masses 202 (unlabelled in plots), 204, 206, 207, 208, and 210 only. In (a) the distribution of channels is the same as for the scanned spectrum of Figure 1 except that only 0.9 amu is included in each peak rather than the full width. In (b) the spacing between channels is the same but only the most intense 0.21 amu has been sampled at each mass. The peak at 204 is higher relative to the other lead peaks by a factor of eight compared to Figure 1 because of the increased fraction of data collection time spent on the minor isotope. The heights of the peaks (vertical scale follows "Int" in upper box) in (b) are ≈ 3 times those in (a) for the same collection time because no time was spent on the low intensity peak sides.

Figure 3

Schematic representations of improperly (a) and properly (b) centered peaks as might occur with the modified peak-centering routine. In (a) using a default mass calibration, the portion of the peaks sampled is to the low mass side of their centers. In (b), a second data accumulation, the information gained in (a) has been used to shift the instrument's mass calibration and the collected peaks are properly centered. In this case, two peaks in (a) were above the threshold and used to determine the mass calibration.

Figure 4

Lead isotopic ratios determined for five analyses of the SRM 981 standard. The 208/206 ratio was used to correct for mass bias. Uncertainties plotted are $1\sigma_m$ for ten one-minute data collections which have been averaged for each analysis. The uncertainty of the 207/206 points are smaller than the symbols. The 207/206 values are in good agreement with the NBS values and fall on the expected horizontal line at unity. The 204/206 data are reproducibly incorrect.

Figure 5

Variation of the 207/206 lead isotopic ratio in SRM 981 as a function of the 206 dwell time when the 207 dwell was

set long (20.5 msec) - squares. The round and diamond points illustrate the effect of varying the fraction of the peak width included in the measured peaks. The 39 point per peak case covered 0.9 amu. The 9 point per peak cases covered 0.21 amu. In all cases, the 208 and 206 dwell times were equal.

Figure 6

Schematic of the operating regions of a quadrupole mass filter. For a given mass; e.g., M_2 , any combination of DC and RF voltages within the shaded area will transmit ions of mass to charge ratio M_2 . In operation a mass spectrum is scanned by varying the voltages linearly. When the resolution is properly set, the voltage ramp will cause mass M_1 to be rejected before M_2 is transmitted. If the slope of the DC/RF ratio, is too shallow the spectrum will be under-resolved. If it is too steep, low transmission will result. In peak jumping, the voltages are stepped along the line of proper resolution, but if data collection starts too soon after a step the DC voltage will lag the RF moving the quadrupole into a zone of higher transmission and lower resolution than anticipated.

Figure 7

Schematic timing diagram. In the "unmodified timing" case, which represents the instrument as supplied, there is only a short time ($\approx 3 \mu\text{sec}$) between data collection in sequential channels of the multichannel analyzer. When the data collection stops for a given channel, the quadrupole control voltages are incrementally changed. As illustrated by the "quad response" curve, the response of the quadrupole to these instructions is slow compared to the inter-channel wait time of the system. We have modified the hardware to introduce an additional wait period before the start of acquisition in each channel. If this interval is properly selected, the quadrupole reaches equilibrium before acquisition begins for the next channel.

Figure 8

Schematic of modification used to achieve channel-by-channel delay of the start of data acquisition by the multichannel analyzer.

Figure 9

Effect of selected acquisition delays on the accuracy of lead isotopic ratios. With a 500 μsec delay out of a nominal dwell time of 640 μsec (140 μsec active), the ratios are still low by $>0.5\%$. The apparent crossover of the 0 and 200 μsec data is assumed to reflect a statistical fluctuation.

Figure 10

Comparison of the precision and reproducibility of multiple analyses of a lead sample. Each point is the average of ten

one-minute data accumulations. The error bars are $1\sigma_m$ uncertainties of the ten accumulations. The scanning data (a) are less precise than the peak-jumping data (b) for the same total data collection time and sample consumption. The reproducibility for repetitive determinations is better for the peak-jumping points as expected from their smaller individual uncertainties. The average value for the peak-jumping determinations is slightly below but within 2σ of the NBS value. In that these peak-jumping data were collected for precision rather than accuracy comparisons, long (>1 msec) dwell times and no delay were used. The low values most likely reflect this fact.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

ICP-MS Interpoint Delay

For MCA Counter Drg # MS741-200D issue 3

Cut Trace To IC 7 Pin 8

G. Hunt
11-17-89

Figure 8

Figure 9

Figure 10

- END -

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