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Maintaining High Resolution Mass Spectrometry Capabilities for National Nuclear Security Administration (NNSA) Applications

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ABSTRACT
The Department of Energy (DOE) National Nuclear Security Administration (NNSA) has a specialized need for analyzing low mass gas species at very high resolutions. The currently preferred analytical method is electromagnetic sector mass spectrometry. This method allows the NNSA Nuclear Security Enterprise (NSE) to resolve species of similar masses down to acceptable minimum detection limits (MDLs). Some examples of these similar masses are helium-4/deuterium and carbon monoxide/nitrogen. Through the 1980s and 1990s, there were two vendors who supplied and supported these instruments. However, with declining procurements and down turns in the economy, the supply of instruments, service and spare parts from these vendors has become less available, and in some cases, nonexistent.

The largest NSE user of this capability is the Savannah River Site (SRS), located near Aiken, South Carolina. The Research and Development Engineering (R&DE) Group in the Savannah River National Laboratory (SRNL) investigated the areas of instrument support that were needed to extend the life cycle of these aging instruments. Their conclusions, as to the focus areas of electromagnetic sector mass spectrometers to address, in order of priority, were electronics, software and hardware. Over the past 3-5 years, the R&DE Group has designed state of the art electronics and software that will allow high resolution legacy mass spectrometers, critical to the NNSA mission, to be operated for the foreseeable future. The funding support for this effort has been from several sources, including the SRS Defense Programs, NNSA Readiness Campaign, Pantex Plant and Sandia National Laboratory.

To date, electronics systems have been upgraded on one development system at SRNL, two production systems at Pantex and one production system at Sandia National Laboratory. An NSE working group meets periodically to review strategies going forward. The R&DE Group has also applied their work to the electronics for a Thermal Ionization Mass Spectrometer (TIMS) instrument, which applies a similar mass spectrometric technology for resolving high mass isotopes, such as plutonium and uranium. Due to non-compete clauses for DOE, all work has been performed and applied to instruments which are obsolete and are no longer supported by the original vendor.

BACKGROUND
The Savannah River Site is a 310 square mile site located near Aiken, South Carolina. The site is owned by the Department of Energy and is primarily managed and operated by Savannah River Nuclear Solutions™, which is a team led by Fluor Corporation,

Newport News Nuclear and Honeywell International Corporation.[1] The primary mission of this DOE site is environmental management, but the NNSA also plays a key role. The NNSA has activities in Defense Programs and Nuclear Non-Proliferation which include operations of the Tritium Facility and start up of the Mixed Oxide Facility (MOX), respectively. The major focus of the Tritium Facility is to manage the Gas Transfer System (GTS) operations, which supports the loading, unloading and surveillance of hydrogen isotopic gases for nuclear weapon components. In order to qualify gases for this focus area, the site must maintain a capability to precisely and accurately analyze low mass gas species at high resolution for use in these components.

INTRODUCTION

The analytical instrument currently utilized to analyze low mass gases to the required accuracy, resolution and sensitivity is the electromagnetic sector mass spectrometer. The key characteristic of this instrument is its capability to resolve species of very similar masses, such at HT and D_2. Common mass spectrometer instruments typically differentiate masses at one atomic mass unit (amu), but HT and D_2 have molecular masses of 4.02388 amu and 4.02800 amu, respectively. The resolution (R) required to distinguish like masses is defined as

$$R = M/\Delta M$$

Where,
M = mass and
ΔM = mass difference (or delta)

Therefore, to be able to measure both HT and D_2 in a gas mixture, the resolution required would be 977. Table 1 lists other potential components and required resolutions.

Ion (positive)	**M/Q**	**Resolution (M/ΔM)**
D^+	2.01400	1221 (D->H_2)
H_2^+	2.01565	
$^3He^+$	3.01603	1580802 (^{3}He-T)
T^+	3.01605	522 (T->HD)
HD^+	3.02183	1831 (HD->H_3)
H_3^+	3.02348	
$^4He^+$	4.00260	188 (^{4}He->HT)
HT^+	4.02388	977 (HT->D_2)
D_2^+	4.02800	
DT^+	5.03005	
T_2^+	6.03200	603 (T_2->D_3)
D_3^+	6.04200	
CO^+	27.9949	2489 (CO->N_2)
N_2^+	28.0062	

Table 1. Masses of typical gas component ions and required separation resolution values

The magnetic sector mass spectrometers at SRS have a resolution around 3,000. In some applications, the resolution may be reduced in order to achieve higher sensitivities.

MAGNETIC SECTOR MASS SPECTROMETER THEORY

The magnetic sector mass spectrometer measures the ions of gas components at a certain position after they have been electrically accelerated into and deflected by an electromagnet which is depicted graphically in Figure 1.

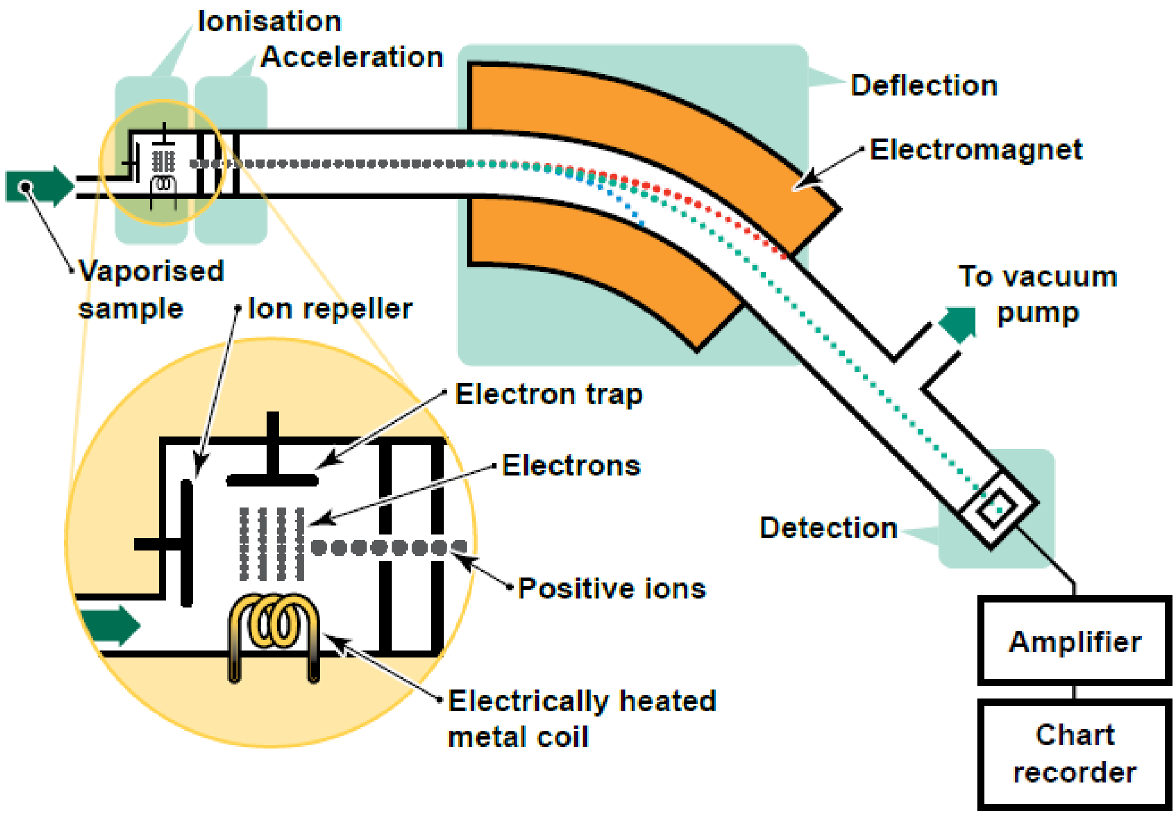

Figure 1. Schematic Diagram of Electromagnetic Sector Mass Spectrometer[2]

A gas sample is introduced into an ionization volume where the components are ionized by a stream of energetic electrons, then accelerated by an ion repeller into a very low pressure flight tube. The ions are focused through a series of charged slits in the flight tube where they enter the electromagnetic field and are deflected, based on their mass and charge, toward Faraday ion collector cups. The magnetic current and the acceleration voltage can be cycled together or separately through a range of values to focus gas component ions to the Faraday cups at specific intervals. Lighter charged ions will be deflected more strongly than heavier charged ions. A typical mass spectrum of ion intensity versus mass/charge is shown below in Figure 2. The various instrument parameters must be tightly controlled to obtain effective results.

The resolution of CO and N_2 is often an issue for various sites to analyze. Any degradation of instrument performance could result in a loss in resolving capability of these species. Figure 3 shows a spectrum with distinct CO^+ and N_2^+ peaks.

The electrons which ionize the gas components in the ion source are subjected to a potential field to optimize the number singly charged ions. Doubly charged ions will be deflected twice as much, which will affect detection sensitivities and interferences. The acceleration voltage out of the ion source is on the order of 10,000 volts, so positions of instrument components are very susceptible to arcing. A typical failure mode of the mass spectrometer is failure of the ion source filament, similar to a common light bulb. Therefore, the filament current is controlled to supply sufficient electrons, but also to realize a reasonable life cycle.

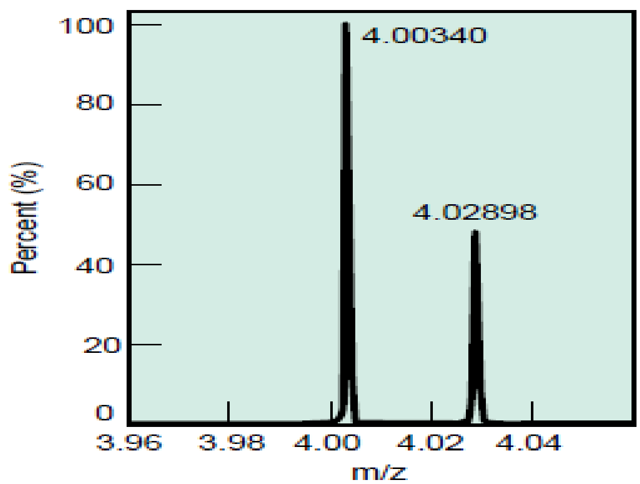

Figure 2. Typical spectrum of hydrogen isotopic gas sample

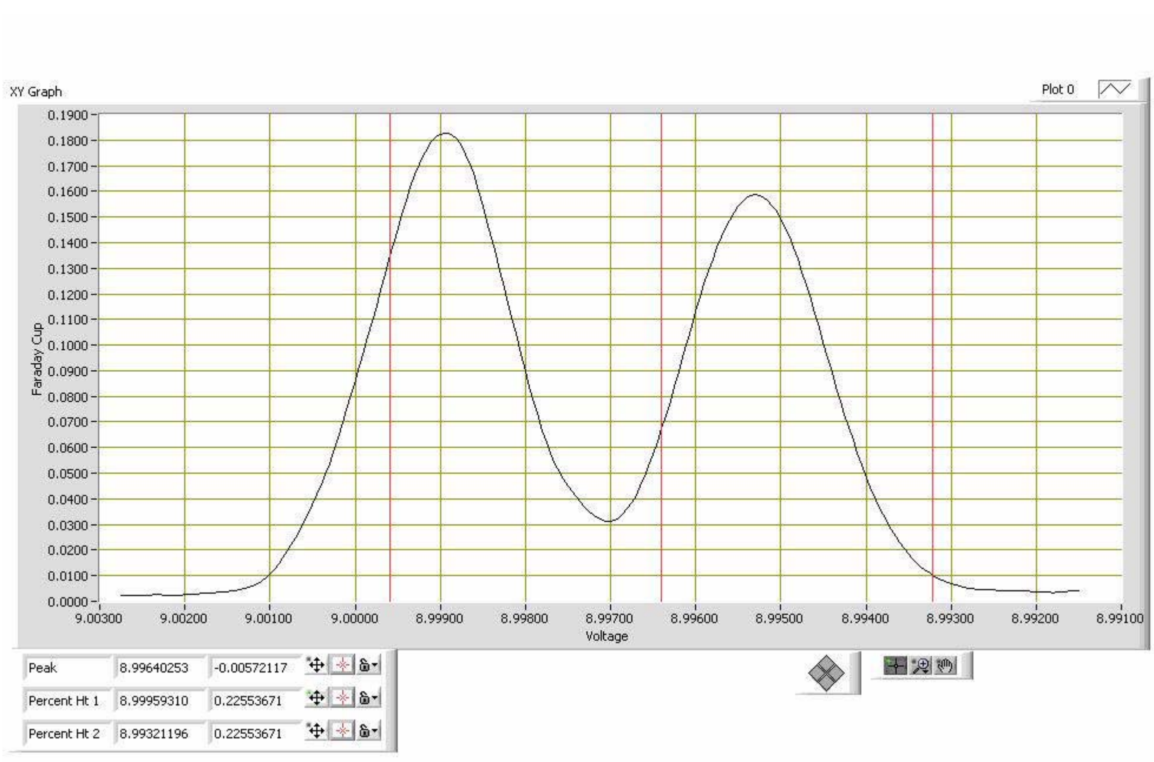

Figure 3. Spectrum of CO and N_2 gas mixutre

There are cases where some species cannot be resolved, such as $^{3}He^{+}$ and T^{+}. One way to account for some interferences is to establish contribution factors. For instance, given a pure T_2 sample, the ratio of the T_2^{+} peak to the T^{+} or T_2^{2+} peak could be examined and a contribution factor could be calculated for future analyses. Also, prior to implementation of this mass spectrometry technology, there were several species that could not be resolved, so other sample handling techniques were employed.

1. Samples which included tritium could use beta scintillation counting to supplement a mass spectrometry analysis.
2. Also, some sample introduction volumes used to include a titanium sublimation pump (TSP) to remove hydrogen components from a gas. Therefore if a sample included D_2 and ^{4}He, the overall mass 4 contribution could be measured. Then, by turning on the TSP, the D_2 would be removed from the gas phase as a metal hydride, so the remaining mass 4 peak would be ^{4}He.

ISSUE

When the electromagnetic sector mass spectrometer technology was introduced to the DOE Complex in the late 1980s and early 1990s, a large number of instruments were purchased, installed and implemented at several sites, including Savannah River Site, Sandia National Laboratory, Pantex Plant, Los Alamos National Laboratory, Y-12 Plant, Mound Laboratory, Lawrence Livermore National Laboratory, Pacific Northwest National Laboratory and the Idaho National Engineering Laboratory. At the time, there were two qualified vendors for the mass spectrometers, Finnigan and VG. Although the two vendors' products were very similar, the VG only focused samples with the electromagnetic current while the Finnigan varied both the electromagnetic current and the high voltage accelerating field. With the large number of instruments being procured, the support from the vendor was more than adequate. However, as procurements started to taper off and the semi-conductor business for other product lines increased, the emphasis on the DOE instruments started to diminish. With a large supply of spare parts and electronic boards available initially, much of the site support would be to change out electronic boards until the problem was addressed, then order replacement boards as necessary. As the support for DOE started to decline, the spare parts availability became limited, and as the instruments aged, they became less reliable. Because of the strict requirements for instrument components and the high voltage being utilized, on-site diagnostic trouble shooting was difficult. When Finnigan and VG announced in the late 1990s that they would stop building new instruments and, in the near future, stop providing support for existing instruments, the NNSA realized that there was a high risk of not being able to sustain the electromagnetic sector mass spectrometer technology. There have been a few small companies trying to provide support, but they typically do not survive long.

ADDRESSING THE ISSUE

The National Nuclear Security Administration (NNSA) started up in the 1990s to actively focus on nuclear issues within the Department of Energy. Within the NNSA, a focus group was formed to address technical issues in the Nuclear Weapons Complex (NWC). This group was named the Network of Senior Scientists and Engineers (NSSE). One of their fist issues to tackle was the electromagnetic sector mass spectrometer issue. In addition, the Gas Technology - Interagency Manufacturers Operating Group (GT-IMOG) was concerned with the mass spectrometry risk and held technology sessions to evaluate it. The NSSE and the GT-IMOG had representatives from across the NNSA sites and were interested in a complex-wide solution. The highest risk issue was determined to be the instrument electronics. At the time of initial implementation of the instruments, the technology was state-of-the-art.

Savannah River Site was the largest player in the electromagnetic sector mass spectrometer business and was willing to expend funding to address the issue. However, because the SRS instruments were all running nearly 24 hours per day, 7 days per week, it was difficult to investigate and experiment with these instruments. Sandia National Laboratory offered one of their Finnigan instruments for development and in return would receive the first upgrade application of the technology.

UPGRADING EXISTING MASS SPECTROMETERS[4]

The SRNL Engineering Team was driven primarily to upgrading these electromagnetic sector mass spectrometers to as good as, or better, quality than the existing technology. A second goal was to use commercially available components to simplify and minimize costs. A third goal was to establish more electrical measurement points to (A) better trouble-shoot instruments when failures occurred and (B) measure trends in specific measurements to provide preventative maintenance, prevent failures and minimize possible instrument downtime. Finally, the fourth goal was to make the instrument more user-friendly, by providing key measurements, but also, by enhancing the software to provide better graphics and easier controls for managing the operation of the instrument.

The Emission Regulator Chassis controls the ionization of the sample and the initial acceleration of the ionized particles into the flight tube. While the potentials and currents in the ionization source are not high, they are operating in a very high potential field, on the order of 10,000 volts. Therefore, this chassis is very susceptible to arcing and must be very carefully laid out. Figure 4 is an SRNL chassis that was part of a VG instrument upgrade for Pantex.

The high voltage power supply was required to have very tight precision, while being capable of adjusting to very small incremental changes in voltage. The SRNL team was able to realize these characteristics by utilizing two 16 bit digital to analog circuits to control the voltage field at 10,000 Volts $\pm$ 0.05 Volts, while still achieving step size increments of 0.0006 Volts.

The magnetic field is measured by a Hall probe, which is inserted into the flight tube in the effective magnetic field. The magnetic field must demonstrate good linearity to the applied electromagnetic current and exhibit a low temperature coefficient. Figure 5 shows the relationship of the magnetic field measured by a commercially available Lakeshore Hall probe in the SRNL development Finnigan mass spectrometer holder.

To address the sensitivity, or detection limits, of the instrument, the SRNL team looked to improve on the Faraday cup amplifier process. They were required to produce the printed circuit boards with matching dimensions while analyzing currents down to $1x10^{-14}$ Amps. This capability was developed previously at SRNL through a Production Directed Research and Develop (PDRD) project for a universal tritium transmitter pre-amp design.

Figure 4. Emission Regulator Chassis

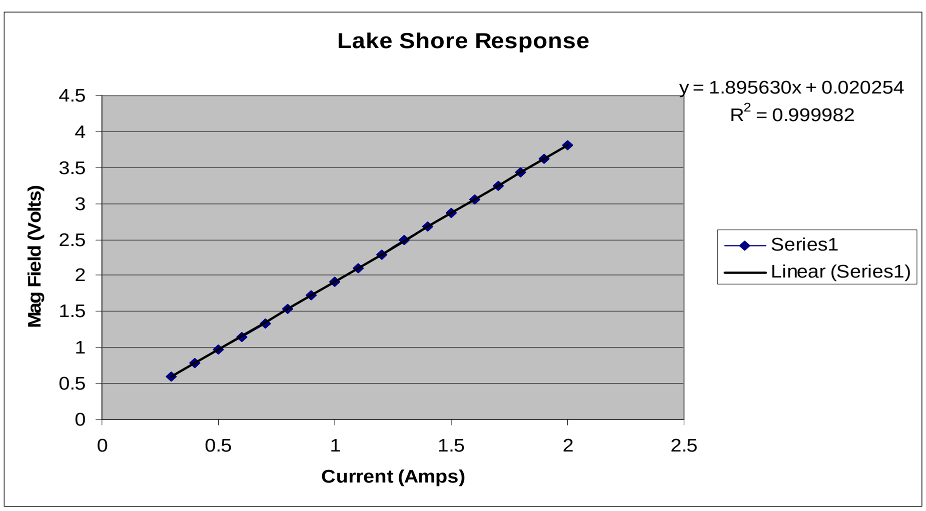

Figure 5. Magnetic Field Probe Response

The SRNL team developed a National Instruments LabView software program which provides executable program controls for electronic settings and data acquisition. The highly improved graphics capabilities greatly simplify operator control of the instrument, while providing visual representation of the current state of instrument parameters. Figure 6 shows the LabView representation of the gas inlet system for the sample introduction process. The valves can be easily operated, as opposed to traditional methods of manual valve operations or even pneumatic valves controlled on a rectangular grid near the computer work station. The software development staff has worked closely with its customers to coordinate existing software applications to accommodate site-specific processes which are in their current, respective procedures.

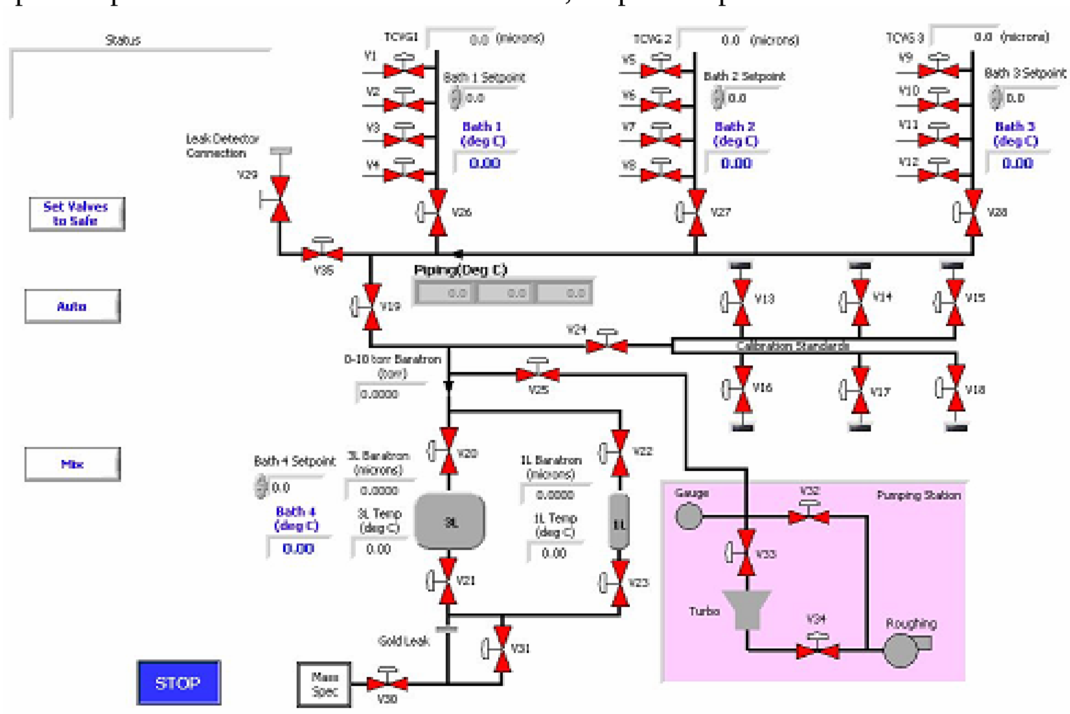

Figure 6. Schematic View of Gas Inlet System with SRNL Developed Software

CONCLUSIONS

The effort to upgrade magnetic sector mass spectrometers in the NSE has not only extended the life cycle of these instruments by at least 10-20 years, it has enhanced the performance, maintenance and ease of use of the traditional instruments. To date, the SRNL team has upgraded two VG instruments at Pantex, one Finnigan instrument at Sandia National Laboratory and one development unit at Savannah River Site. Additionally, the SRNL team has successfully repaired and upgraded a Finnigan Thermal Ionization Mass Spectrometer (TIMS) at the Savannah River Site F/H Area Production Support Laboratory, used to measure uranium and plutonium isotopic ratios, for trans-uranic material processing.

Figure 7 gives a holistic representation of the magnetic sector mass spectrometer system. The control computer is essentially the brain which communicates instructions, operates valves, acquires data and visually shows the working relationship of all instrument parts.

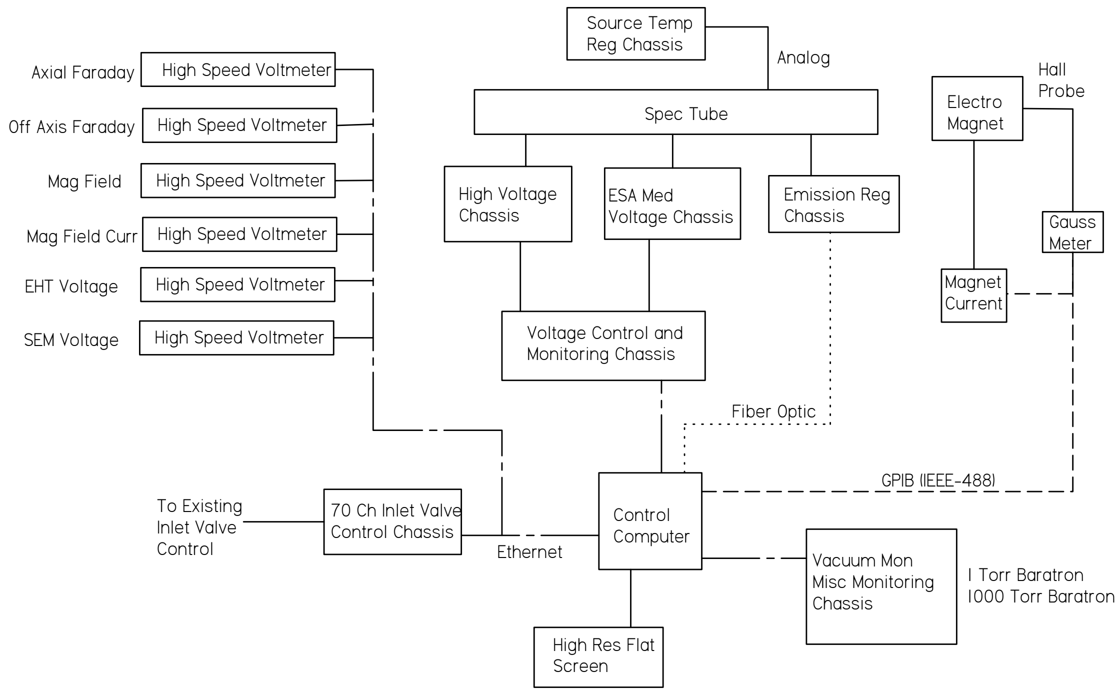

Figure 7. Mass Spectrometer Block Diagram

Figure 8 shows final upgraded mass spectrometer system at SRNL. This instrument was provided by Sandia National Laboratory and has allowed the SRNL team to move forward as a very fast pace. While there are quite a number of instruments at SRS, they are not readily accessible for development work because of the high demand placed on them by operations. The Sandia furnished instrument has accelerated the development of the mass spectrometer upgrade by at least five years.

Figure 8. Upgraded Finnigan SRNL Mass Spectrometer

FUTURE CHALLENGES

The SRNL team will continue to support existing systems they have upgraded at the various sites. NNSA will continue to hold technical discussions with the NSE mass spectrometer community. Sandia has an open procurement with SRNL to provide technical support, as necessary. Pantex has requested SRNL to upgrade a Finnigan instrument at their site. Previously, SRNL upgraded two VG instruments at Pantex, so the Finnigan upgrade will include new implementation requirements.

In addition to the progress that has been made in developing electronics and software upgrades for the mass spectrometer systems, a new effort is being pursued to address hardware support and upgrades. Specifically, SRNL is looking into investigating flight tube and electromagnet characteristics. New Brunswick Laboratory (NBL) has recently proposed to transfer a Finnigan electromagnetic sector instrument to Savannah River Site for further R&D development activities. This mass spectrometer was previously used at the DOE Mound Laboratory in Miamisburg, Ohio, in support of the tritium programs. The Mound Laboratory was shut down in the mid 1990s and the instrument was decontaminated and shipped to NBL in 2002. The current plan is to transfer the instrument to SRS, cut sections of the flight tube and attempt to reverse engineer a replacement flight tube for NNSA obsolete systems. Additionally, some of the parts of the NBL system will be set up for potential spare parts.

The electromagnet is also a key component of the mass spectrometry technology. SRNL has been communicating with Sandia National Laboratory, other DOE Laboratories and private sector companies to investigate a potential electromagnet replacement processes.

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