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TRITIUM ANALYSIS AT TFTR

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ABSTRACT

The tritium analytical system at TFTR is used to determine the purity of tritium bearing gas streams in order to provide inventory and accountability measurements. The system includes a quadrupole mass spectrometer and beta scintillator originally configured at Monsanto Mound Research Laboratory in the late 1970's and early 1980's. The system was commissioned and tested between 1991 and 1992 and is used daily for analysis of calibration standards, incoming tritium shipments, gases evolved from uranium storage beds and measurement of gases returned to gas holding tanks. The low resolution mass spectrometer is enhanced by the use of a metal getter pump to aid in resolving the mass 3 and 4 species. The beta scintillator complements the analysis as it detects tritium bearing species that often are not easily detected by mass spectrometry such as condensable species or hydrocarbons containing tritium. The instruments are controlled by a personal computer with customized software written with a graphical programming system designed for data acquisition and control. A discussion of the instrumentation, control systems, system parameters, procedural methods, algorithms , and operational issues will be presented. Measurements of gas holding tanks and tritiated water waste streams using ion chamber instrumentation are discussed elsewhere.[1,2]

I. INTRODUCTION

The U.S. Department of Energy (DOE) requires that tritium be accurately quantified as it is moved from site to site, and in the case of PPPL as it moves within the bounds of the laboratory for experiments on TFTR. Most of the measurements involve pressure, volume and temperature determinations of the quantity. The purity of gas in each aliquot is typically determined by quantitative mass spectrometry and beta scintillation measurements. Monsanto Mound Research Laboratory was contracted to provide the system for storage, delivery and analysis of tritium at PPPL. This work started in the latter part of 1978. Glove boxes and tritium handling equipment were designed, constructed, tested and delivered to PPPL in 1981. A prototype for the analysis system was described by Dylla and Ellefson.[3] An Extranuclear QPS mass spectrometer was partially installed in 1988 but not commissioned until nearly 4 years later. An Analytical Devices beta scintillator detector was also included in the system but was found to be defective and unsupported by the original vendor. EG&G Mound Laboratory provided a redesigned instrument that was installed in 1991. A final enhancement to the hardware was the inclusion of a metal getter pump to aid in resolving mass to charge (m/q) 3 and 4 species. Initial testing was performed using pure gases and non tritium bearing mixtures of hydrogen and deuterium. Testing of the system with tritium was first conducted in May of 1993 when PPPL received authorization from DOE to proceed with tritium operations.

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[1] N.P. Kherani, W.T. Shmayda, 'HTO Monitoring Using Heated Ion Chambers,' 15th IEEE/NPSS Symposium on Fusion Eng., 80, (1993).

[2] LaMarche, et al. , Proceedings ANS, 1994 New Orleans, La. (to be published).

[3] R.E. Ellefson, W.E. Moddeman, H.F. Dylla, J. Vac. Sci. Technol., **18**, 1062 (1982)

MW

II. EQUIPMENT

A. QMS

The Extranuclear quadrupole mass spectrometer consists of a quadrupole filter with 9.5 mm diameter rods run at 5.1 Mhz. Ions are produced by an axial electron impact ionizer which was modified to include dual, remotely selectable tungsten filaments to minimize downtime in the event of a filament failure. The electron energy is set at 70 eV with an emission current of 0.85 mA. Ion energy is 10 eV. Ions are detected by a Gallileo channel electron multiplier typically operated at 2000 volts. The faraday cup detector is not used for daily measurements. The generated ion current passes through one of 3 input resistors in the electrometer: $10^6\Omega$, $10^7\Omega$, or $10^8\Omega$. The original equipment was modified to allow remote selection of the input resistor via computer. The instrument has a mass range of 70 AMU with resolution at the 10% peak level of 2. An upgrade to the electronics is scheduled for the early part of 1995. At that time the mass range should extend to nearly 150 AMU.

B. Beta Scintillator

The original Analytical Devices Model 120D beta scintillator exhibited unacceptable drift during the commissioning period and was replaced by an EG&G Mound Laboratory redesign. A CaF2 (Eu doped) crystal is immersed in the sample gas and fluoresces due to the beta decay particles of tritium and tritium bearing compounds. Photons are detected by an electron multiplier tube whose output stages are tied together. The output current is measured by an electrometer whose output ranges from 0 to approximately 12 volts. The usable pressure range of 0 to 1 torr is limited by the range of the Baratron™ pressure transducer. This is not a serious limitation, however, since absorption of the beta decay particles becomes a problem at pressures above 3 torr. The electrometer signal is converted to a 4-20 mA current which is input to the Tritium Remote Control and Monitoring System (TRECAMS) and a Macintosh II Ci computer used for data acquisition.

The mole percentage of tritium in the sample is determined by the following equation:

$$T_2(\%) = 100\,K\,\frac{\Delta Signal}{\Delta \mathrm{Pr}essure} \tag{1}$$

Where:

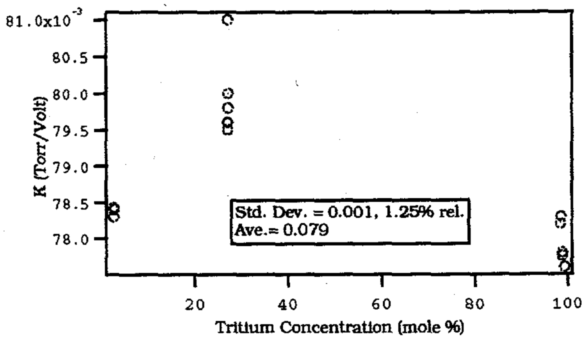
K= beta scintillator sensitivity in (Torr/Volt)

ΔSignal = signal with sample gas present minus signal without gas (Volts)

ΔPressure = Pressure with sample gas minus pressure without gas (Torr)

The linearity of the device was tested at Mound using a calibrated LED monitored by a Minolta L-110 Spot Photometer. The coefficient of linear response was shown to deviate by ≤0.09%. [4] The uncertainty of the slope of the response curve was less than 1.4%. These measurements were not repeated at PPPL.

The value of K is determined by noting the response of the instrument to known standards. The value of K vs. tritium concentration in known standards is shown in figure 1. The average value at maximum gain level is 0.079 with a standard deviation of 0.001 determined by analyzing data over a several month period. This is 4 to 5 times higher than the values measured at Mound using the prototype. This difference is partially due to the additional signal conditioning between the beta scintillator and the acquisition system at PPPL.



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[4] Beta Scintillator Mode MD-200 Operating Manual (EG&G Mound Applied Technologies) Feb. 1993.

Fig. 1 Beta Scintillator K value vs. tritium concentration

Noise levels are determined by observing the standard deviation of the 'zero' level over 500 measurements. The 3 sigma level is typically 0.008 volts. This yields a detection limit of 0.06%. This value is also consistent with the value of ~0.08 % due to 2 bits of uncertainty in the 12 bit analog to digital converter.

C. Metal Getter Pump

A metal getter appendage pump containing SAES type 707 alloy[5] (Zr-Vn-Al) is typically used in the second phase of analysis to discriminate between inert species and active species at m/q of 3 & 4. The matrix is normally heated to 150°C to maintain an active metal surface. The remaining gas after the active portion of analysis is complete is brought in contact with the getter. The residual gas at the conclusion of the gettering process is typically composed of inert species. The pump is regenerated approximately every two weeks by raising the temperature to 500°C while maintaining a vacuum. The accumulation in the pump is typically 25 to 50 curies.

III. CONTROL

A Macintosh II Ci personal computer is used to control the mass spectrometer and acquire analysis data. A National Instruments Lab-NB multifunction card with 8 single ended analog input channels (ADC), 2 digital to analog output channels (DAC) and three 8 bit control words is installed in the Nubus slot of the computer. The ADC & DAC have 12 bit resolution and are configured for unipolar signals between 0 and 9.97 volt DC. Five of the eight input signals are used for the electrometer signal, pressure of the beta scintillator, pressure of the 2 liter batch volume, the beta scintillator signal and status of the inlet valve to the instrument. One of the 2 DAC channels is used to provide the driving signal for the mass scan. Two bits of one of the control words are used to select the electrometer input resistor value. All of the manual controls of the ionizer and quadrupole control are logged on simulated front panels and stored with the data file for each analysis. In addition the parameters for calibration are stored along with the raw data acquired from each analysis.

As well as controlling the hardware the acquisition software guides the operator through the necessary sequence of events and generates and displays analysis reports. A number of utility options allow for calibration and review of archived data. The software is a custom application coded in National Instruments LabVIEW® (Laboratory Virtual Instrument Environment Workshop). LabVIEW® offers an innovative programming methodology in which software modules, or virtual instruments (VI) are graphically assembled. The VIs are built to acquire data from plug-in boards and programmable instruments. The signals are then analyzed and the data is presented through graphical user interfaces. The selection of parameters is made via software front panel devices such as knobs, buttons, dials and menus. The monitoring of processes is via gauges, meters and strip charts; results are reported with graphs, tables and charts. All data is archived to hard disk and later transferred to other computers for long term storage or post processing for trends or review.

IV. QUANTITATIVE ANALYSIS

In order to achieve accurate quantitative analyses a number of factors are considered during the mass scan and subsequent analysis.

- The background of the instrument and sample system contributions due to outgassing and throughput leakage.
- Compensation for the beta shift of the baseline.
- Fractionation of the sample gas as it flows from the 2 liter batch volume into the QMS under molecular flow.
- Fragmentation of the sample in the ionizer (cracking pattern). Data is acquired by scanning from lowest mass to highest. Calculations are made from high mass to lowest mass so that the sum of fragments due to higher mass species can be subtracted.
- The sensitivity of the instrument for each of the expected species.

All of these factors are addressed by the computer control program and by operator input at key times during the analyses.

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[5] SAES Technical note

V. SAMPLING OPERATION

Samples are drawn from various locations via capillary lines. A total of 15 sample points are tied to the analysis system: non-tritium calibration rack (6), incoming tritium sample line (1), Gas Holding Tanks (2), grab sample port (1), tritium standard mixtures (2), Ubed manifold (1), delivery manifold (1) and the secondary containment of the Ubeds (1). Prior to drawing an aliquot of gas the sample manifold, batch volume and getter pump are evacuated and the 'zero' pressure recorded. The beta scintillator baseline value and the QMS baseline at mass 10 are acquired. Mass 10 is chosen because there are no expected peaks at that value and any shift in the detector baseline can be assessed. The turbo molecular pump on the sample tree is isolated for a period of time consistent with a typical sample draw time. The background scan is then taken with the inlet valve to the QMS open. This scan compensates for any throughput leakage or outgassing from the sampling system as well as the background of the QMS chamber. The first aliquot of each sample is purged through the turbomolecular pump for a period of time that results in at least a 3 volume exchange of gas based on viscous flow through the nominal 0.3 mm diameter capillary. This assures that the gas is representative of the actual sample rather than the prior contents of the capillary. The 200 cc sample manifold or 'tree' is filled to a pressure between 0.7 and 1.0 torr. This gas contacts the beta scintillator detector and produces a signal proportional to the partial pressure of tritium in the gas. Next, the 2 liter batch volume is filled to a target pressure of 0.3 torr. When the inlet valve to the mass spectrometer is opened the computer records time zero. Sample gas is introduced into the QMS under molecular flow through a 5 hole leak foil. Pressure in the QMS vacuum chamber reaches approximately 5 x 10^{-5} torr at the start of analysis. The exponential decay of pressure in the batch volume is subject to fractionation proportional to mass by the following equation:

$$P(t) = P_0 e^{\frac{-L(t-t_0)}{\sqrt{m}}} \tag{2}$$

Where:
L= molecular leak rate in AMU $^{1/2}$ Sec^{-1}
P= pressure in torr
t= time in seconds
m= mass of species in amu

The QMS scans and integrates ± 20 digital points around each peak 4 times and calculates the average and standard deviation of that signal. The typical spacing between masses is 51 digital points. The electrometer input resistor is initially set to $10^8\ \Omega$ for each peak, the most sensitive range. In the event that the peak overranges the analog input (typically 9.97 volts) the next lower resistance is selected and the scan of that particular peak is repeated. There is provision to measure only selected peaks. At the conclusion of the active phase of the analysis the spectrum is corrected for background and baseline beta shift, exponentially corrected for fractionation to time zero and finally corrected for fragmentation from higher mass species.

Corrected Peak =

$$\left(Pk_i - Bk_i - \Delta Bs\, e^{\frac{-Lt_i}{\sqrt{6}}}\right) e^{\frac{+Lt_i}{\sqrt{m_i}}} - Int \tag{3}$$

Where:
Pk_i= the uncorrected peak at m/q = i (amp)
Bk_i= the background signal at m/q=i (amp)
Bs= the net baseline value at m/q=10 (amp)
m_i= m/q (amu)
L= molecular foil leak rate (amu $^{1/2}$ sec^{-1})
t_i=elapsed time after inlet valve is opened (sec)
Int= cracking interferences from higher mass species (amp)

A prompt directs the operator to manually open the isolation valve for the metal getter pump. When the reduction in pressure due to gettering is complete the operator strikes a key on the computer and a second scan commences. This 'inert' scan is background, fragmentation and fractionation corrected and is used predominantly to resolve the conflicts at m/q = 3 and 4. Typically the residual is the inert component of the sample gas, i.e., Ar, ^{3}He, ^{4}He and Ne as well as a small amount of the N_2 component which has a lower gettering efficiency than the hydrogen species.

At the conclusion of the mass scan the partial pressure of each species is determined by dividing the corrected peak signal by the sensitivity for that species. An algorithm[6] applies to the interpretation of ^{3}He from HD and the separation of ^{4}He from D_2 and HT. The partial pressure for ^{3}He is simply the inert value at mass 3 corrected to time zero. HD partial pressure is the difference between the active value at mass 3 and the inert value just determined. Similarly, the ^{4}He partial pressure results from analysis of the mass 4 inert. The remainder formed by subtracting this amount from the active value at mass 4 must be apportioned to HT and D_2. Separation of HT and D2 requires making some assumptions and calculations based on expected abundances of HD, DT and T2 in isotopic equilibrium. Based on equilibrium conditions there are two equations that can be used to separate HT & D_2. A 30% total tritium level is used as a breakpoint in deciding which calculation method is to be used via the following test:

If
$$\frac{\left[PP(T_2)+\frac{PP(DT)}{2}\right]}{P_{inlet}} > 0.3 \tag{4}$$

Then
$$PP(D_2)=\frac{\left[PP(DT)\right]^2}{3.82\times PP(T_2)} \tag{5}$$

and
$$PP(HT)=PP(HT+D_2)-PP(D_2) \tag{6}$$

Note: if
$$PP(HT)<0 \tag{7}$$

Then define
$$PP(HT)=0 \quad \text{and} \tag{8}$$

$$PP(D_2)=PP(HT+D_2) \tag{9}$$

If
$$\frac{\left[PP(T_2)+\frac{PP(DT)}{2}\right]}{P_{inlet}} < 0.3 \tag{10}$$

Then
$$PP(HT)=\frac{1.74\times PP(HD)\times PP(T_2)}{PP(DT)} \tag{11}$$

and
$$PP(D_2)=PP(HT+D_2)-PP(HT) \tag{12}$$

Note: if
$$PP(D_2)<0 \tag{13}$$

Then define
$$PP(D_2)=0 \quad \text{and} \tag{14}$$

$$PP(HT)=PP(HT+D_2) \tag{15}$$

Where:
Pinlet= pressure in the expansion volume at time zero (Torr)
PP(X)= partial pressure of species X (Torr)

Note that the equation for partial pressure of D_2 can become undefined for T_2=0. A special case is used in the analysis if the concentration of T2< .1 mole %. The contribution to HT is assumed to be negligible and all of the active scan at m/q=4 is taken as D_2 .

With the exception of condensable species the calculated partial pressures are summed and compared to the pressure in the batch volume at time zero. The ratio of calculated to measured pressure (C/M) provides a figure of merit or closure for the analysis. A value of 1.0 is a good indication that the sensitivities were correct and that all species were properly accounted. In general, if the C/M value for an analysis falls within 10% of unity it is considered valid. Analyses that fall outside that range flag the need for adjustment of sensitivities or the need to examine the spectrum more closely for anomalies.

VI. CALIBRATION

A suite of calibration gases are available for confirmation of the instrument performance. Control charts are updated daily in order to track measured values minus standard values

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[6] Correspondence with David Cain and Robert Ellefson of EG&G Mound Laboratory (1993)

vs. time. These charts are published quarterly in a measurement control report which is submitted to the site Nuclear Material Custodian (NMC). Figures 2 & 3 are examples of control charts for a 6 month period showing the difference of the measured value minus the standard value for the nominal 30% tritium standard. Superimposed are the average and ±3 sigma value.

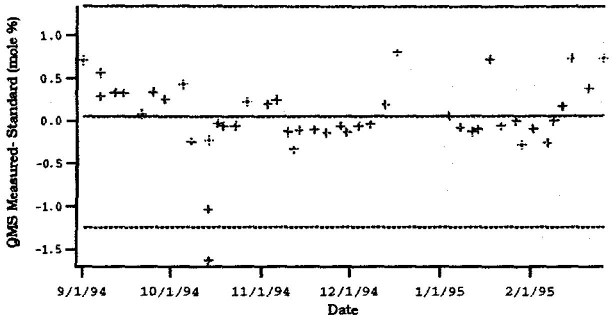

Fig. 2 Control Chart for QMS of 30% Tritium Standard

Non tritiated calibration gases include H_2, D_2, Ar, ^{3}He and mixtures ^{4}He/ N_2 50% each component, a six component mixture consisting of H_2, D_2, ^{4}He, Ne, N_2 & Ar at equal levels, an HD mixture and several mixtures of components such as CH_4 or SF_6 and O_2 in a balance of N_2. There are two tritium calibration standards: a nominal 3% and 30% mixtures of T_2 in D_2 prepared by Westinghouse Savannah River Site.

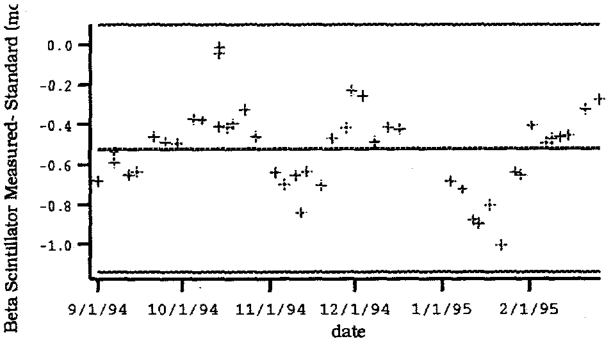

Fig. 3 Control Chart for Beta Scintillator of 30% Tritium Standard

Sensitivities are checked and adjusted regularly. A variation in the *C/M* value of greater than 10% is corrected by scaling based on the *C/M* figure. For changes greater than 25% a retune of the instrumentation is generally performed. This usually forces a redetermination of sensitivities for all species for which there exists a standard and extrapolation of values based on trended ratios for all others.

The molecular foil leak rate is measured several times a year using D_2 to verify the foil's integrity.

Fragmentation patterns are calculated by observing spectra of pure gases and known mixtures.

The volume ratio was measured to correct for the reduction in signal due to pressure drop when the batch volume is opened to the getter pump. This forms a correction to the calculation of the mass 3 and 4 inert species.

VI. OPERATIONAL ISSUES

Normal operations consist of a multitude of analytical activities. These tasks range from daily calibration procedures to assays of incoming shipments, deliveries to the tokamak and inventory determinations of gas holding tanks. The sampling schedule provides for a complete rotation of standards and mixtures in the course of each week.

An analysis of one or both gas holding tanks is performed for inventory purposes daily. Mass spectrometric analysis is used to support the ion chamber measurement of tritium activity by correcting the ion chamber response to different gas species. The gas holding tanks contain a wide range of effluents from TFTR and as such tend to affect the QMS ion source filament which is usually exposed to highly reducing gases. Samples pass through 25 meters of capillary line which may distort the analysis if condensable species precipitate out.

One of the most critical operations is the analysis of incoming tritium shipments and determination of purity of tritium extracted from the Ubeds and delivered to the tokamak. These measurements provide necessary information to determine inventory differences. Shipper-receiver differences have typically under 0.5 %.

Many of the problems that have been encountered to date were the result of failed electronic components many of which were purchased in the early 1980's Shorted electrolytic capacitors have led the list of failures. Most of these have been replaced and spare circuit boards are now available to minimize turnaround time. An upgrade to more recent Extrel electronics has been purchased and software changes and preparation for an exchange are progressing. This upgrade should provide a more stable operating regime and extend the operating mass range to nearly 150 AMU.

One of the problems encountered in the gas holding tanks was the appearance of SF$_6$ and related impurities from regeneration of neutral beams. The QMS was unable to detect the SF$_6$ in the concentrations in the tank because of the limit of 70 amu operating mass range. A standard of approximately 1000 ppm SF6 in N$_2$ was run and the SF$_6$ fragments were still not detected. A gas chromatograph has been purchased which will easily detect this level of impurity in the gas holding tanks.

Long term drift in the instrument sensitivities is such that adjustments need to be made to the calibration file on average every 2 weeks. The short term drift in the instrument is generally several per cent and caused by changes to the filament efficiency following analyses of oxidizing samples.

VII. CONCLUSION

The tritium analytical system at PPPL is routinely used to make the critical measurements necessary for inventory calculations. A well tested system is now in place for maintaining measurement control of the mass spectrometer and beta scintillator. Future enhancements to the system, including the addition of a gas chromatograph will increase the ability to characterize the content of gas streams from many key sources.

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