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ICP-MS Nebulizer Performance for Analysis of SRS High Salt Simulated Radioactive Waste Tank Solutions (#3053)

by

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ICP-MS NEBULIZER PERFORMANCE FOR THE ANALYSIS OF SRS HIGH SALT SIMULATED RADIOACTIVE WASTE TANK SOLUTIONS

REFERENCE: Jones, V.D., **"ICP-MS Nebulizer Performance For The Analysis Of SRS High Salt Simulated Radioactive Waste Tank Solutions"**, Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations: Second Volume, ASTM STP 1344, R.W. Morrow and J.S. Crain, Eds., American Society for Testing and Materials, 1988.

ABSTRACT: High Level Radioactive Waste Tanks at the Savannah River Site are high in salt content. The average Total Dissolved Solids (TDS) content is approximately 25%. For ICP-MS optimum signal stability and to reduce blockage of nebulizers and sampling orifices, it is usual to limit analyte solutions to a TDS content of nominally < 0.2%. Dilution to this level to reduce the matrix effect may push some analytes of interest below detectable levels. Five commercially available nebulizers were evaluated for their performance in a high salt matrix. The nebulizers surveyed were a meinhard concentric, cross-flow, micro-concentric (MCN), v-groove, and a direct injection nebulizer (DIN). Analytes spiked into non-radioactive diluted salt solutions ranging from nominal 0.25 - 1.0 % TDS were repetitively analyzed with the goal of determining stability of response signal and magnitude of any signal loss/suppression resulting from the diluted salt matrix. The cross-flow nebulizer provided the most stable signal for all salt matrices with the smallest signal loss/suppression due to this matrix. The DIN exhibited a serious lack of tolerance for TDS; possibly due to physical de-tuning of the nebulizer efficiency.

Keywords: Inductively coupled plasma mass spectrometry; high salt matrix; meinhard concentric nebulizer, cross-flow nebulizer, micro-concentric nebulizer, v-groove nebulizer, direct injection nebulizer; signal loss and/or suppression

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The Savannah River Site (SRS) located in Aiken, SC is operated by Westinghouse Savannah River Company under contract with the U.S. Department of Energy. Some of the waste currently being stored at the SRS in large underground tanks is high level

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radioactive salt solutions. The average Total Dissolved Solids (TDS) content is approximately 25%. For ICP-MS (Inductively Coupled Plasma - Mass Spectrometry), it is usual to limit analyte solutions to a TDS content of nominally < 0.2% (1). Dilution to this level may push some analytes of interest below detectable levels. The five nebulizers were evaluated for their effect on signal loss/suppression and precision of analyte signal in the presence of salt matrices. This evaluation was performed on a Hewlett Packard 4500 using non-radioactive simulated dilute High Level Waste tank solutions ranging in approximate dissolved solids content of 0.25 - 1.0 %. The purpose being to determine the best nebulizer for this matrix based upon an acceptable signal reduction/suppression at the minimum dilution. An acceptable level of signal reduction/suppression for an internal standard was taken to be ≤ 40% based upon EPA method 200.8 (2).

Most nebulizer evaluations in the literature are carried out individually with comparison to another conventional pneumatic nebulizer (i.e. - concentric, cross-flow or V-groove). To the authors knowledge, there has been no published study of the 3 most widely used nebulizers and 2 specialty nebulizers on high salt matrices on the same instrument and operating conditions. This study seeks to underpin the knowledge base of several commercially available nebulizers for ICP-MS with specific focus on the analysis of high salt matrices for radioactive waste characterization.

Experimental Method

Test Procedure

An HP-4500 ICP-MS (Hewlett Packard, Wilmington, DE, USA), was used to analyze the control standard and matrix test samples. The quadrupole mass analyzer was operated in the peak hopping mode while ion signals were detected by either pulse counting or analog signal dependent upon intensity; with an integration time of 0.33 sec. each and 3 repetitions per mass. A pulse to analog signal calibration (P/A factor) was performed prior to data acquisition using a 100 µg/L control standard at the masses designated for analysis.

The five nebulizers and accessories used were: a meinhard-type (MN) concentric (Meinhard, Santa Ana, CA, USA); cross-flow (CFN), v-groove (VGN) from Hewlett Packard; microconcentric (MCN) and direct-injection (DIN) autosampler (CETAC Technologies, Omaha, NE, USA). An ASX-500 autosampler (also supplied by CETAC) was used with the following sequence: 60 sec. sample flush, 30 sec. equilibration, and following analysis, a 60 sec. rinse in 1% HNO_3. An ASX-100 autosampler was used with the MCN.

To reduce the number of variables, the plasma parameters where minimally adjusted for optimum use of the individual nebulizers (Table 1). RF power was set at 1230 W (exception for CFN). Sample depth was set at 7 mm which was found by Hedrick of Hewlett Packard (3) to be the optimum position for the HP 4500 with high solids. An increased sampling distance allows longer residence time in the plasma and thus greater ionization while shorter sampling distances increase the sample and skimmer cone temperatures reducing the build up of material on cone surfaces. Carrier and blend gas flows as well as lens voltages were optimized for each nebulizer using a 10 ppb tuning solution of Li, Y, Ce and Tl.

TABLE 1 – *Instrument parameters*

	MN	CFN	MCN	VGN	DIN
Salt Matrix	0.28, 0.56, 1.12%	0.28, 0.56, 1.12%	0.28, 0.56, 1.12%	0.28, 0.56, 1.12%	0.28, 0.56, 1.12%
Date	Dec-96	Dec-96	Jan-97	Feb-97	Apr-97
RF Power	1230 W	1200 W	1230 W	1230 W	1230 W
Sample Depth	7 mm	7 mm	7 mm	7 mm	7 mm
Carrier Gas	1.2 L/Min	1.0 L/Min	0.94 L/Min	1.2 L/Min	0.35 L/Min
Blend Gas	0.0 L/Min	0.27 L/Min	0.39 L/Min	0.07 L/Min	0.0 L/Min
Peripump	0.1 rps	0.1 rps	0.1 rps	0.1 rps	0.0 rps
s/c Temp	2 oC	2 oC	2 oC	2 oC	NA
EM Voltage	(-)2010 V	(-)2010 V	(-)2010 V	(-)2010 V	(-)2100 V
Neb Press.					75 psi
GDP Press.					300 psi

The study solution was a simulated representation of the average waste tank matrix containing approximately 28% total dissolved solids. Table 2 lists the contents of this salt solution. All the chemicals used to make the simulated waste were of analytical-reagent grade.

TABLE 2 – *Waste tank simulant*

Average Waste Tank Simulant (~ 28% TDS)			
Na^+	5.00 M	SO_4^{2-}	0.13 M
OH^-	1.45 M	Cl^-	0.02 M
NO_3^-	1.86 M	F^-	0.01 M
NO_2^-	0.73 M	PO_4^{3-}	0.01 M
CO_3^{2-}	0.16 M	$C_2O_4^{2-}$	0.01 M
AlO_2^-	0.29 M		

For dilution of the simulated waste, aliquots were delivered with an electronic pipette (EDP Plus, Rainin Instruments, Woburn, MA, USA). Upon dilution, the test salt solutions contained 100 µg/L each of Sc, Y, In and Tb (as typical internal standards), and 1% v/v nitric acid (Fisher Scientific, OPTIMA grade, Pittsburgh, PA, USA) in 18 MΩ cm water (from this point forward called 'dilute salt'). Three dilution schemes were used resulting in dilute salt TDS content of 0.28, 0.56, & 1.12%. An acid blank of 1% v/v

HNO_3 also containing Sc, Y, In, and Tb at the 100 µg/L level was also prepared and will from this point forward be called the 'control standard'.

For each of the nebulizers, the control standard was analyzed several times to obtain a reference response for each analyte with no salt matrix present. The dilute salt solutions were then analyzed repetitively to measure the degree of matrix effect. Subsequent to the dilute salt analyzes, the control standard was again analyzed several times to look at system recovery and instrument drift over the course of the analyses. Nebulizer data was tabulated for precision of dilute salt analyzes and % drop in average signal due to the combined matrix effect of sample loss and signal suppression. This study did not attempt to differentiate between signal loss and suppression.

All of the data is represented graphically. For summary statistics, terbium was selected overall to compare the nebulizers for the possible application of actinide analyses in salt matrix. Of the internal standards selected, terbiums ionization energy is closest to U (565 vs. 584 kJ/mol (4) respectively).

Signal drop is expressed as

$$\%D = [(SM_{avg.} - CT_{avg.}) / CT_{avg.}]\, 100 \qquad (1)$$

where

$\%D$ = percent signal drop
$SM_{avg.}$ = salt matrix average response
$CT_{avg.}$ = control standard average response

In this way, instrument drift was conservatively compensated for by averaging the control std. analyses that bracket the salt matrix analyses. It is understood that this number could be biased low if partial blockage of the sample cone has occurred during the course of the analyses. However, the slope of the control std. analyses before the matrix analyses gives an extrapolated indication of where the control acid analyses after running the salt matrix should be due to instrument drift alone.

Results

Meinhard Concentric

The meinhard concentric nebulizer used was the 'type A' which is not the optimum for high solids. Chart 1 below shows the signal responses for analysis of 0.28%, 0.56%, and 1.12% TDS salt matrices; each bracketed by analyses of the control standard. All analyses were performed on the same day. Twenty-five replicate analyses were performed for each salt matrix. The 0.28% TDS matrix was the only one evaluated that had ≤ 40% signal drop using the type A meinhard nebulizer.

CHART 1 – *Meinhard concentric high TDS response*

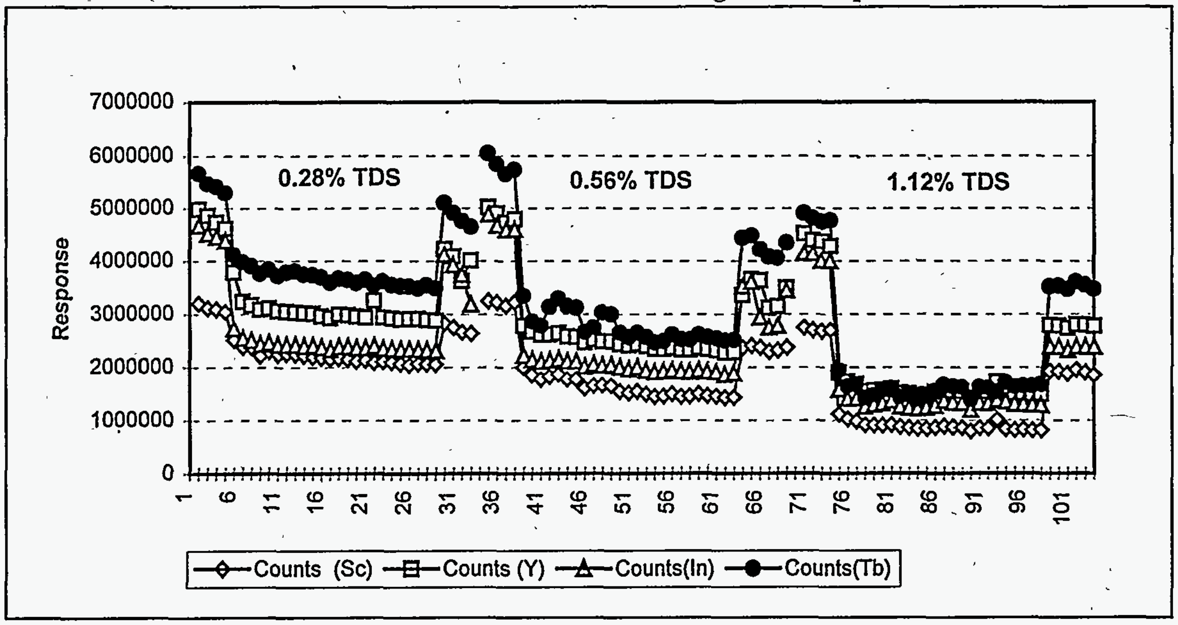


TABLE 3 - *Meinhard concentric data summary for Tb*

Data Summary	Tb, 0.28% TDS	Tb, 0.56% TDS	Tb, 1.12% TDS
Average	3698290	'2756485	1582921
STD @95% CL	331953	575057	255561
RSD @95% CL	9.00%	20.90%	16.10%
% Signal Drop	-28.40%	-43.66%	-60.82%

Cross-Flow Nebulizer

For the cross-flow nebulizer, the RF power was reduced to 1200 W as this produced a more stable response signal. Chart 2 shows the signal responses for analysis of 0.28%, 0.56%, & 1.12% TDS salt matrices; each bracketed by analyses of the control standard. Analyses were performed on 3 non-consecutive days. Twenty replicate analyses were performed for each salt matrix. All of the dilute salt matrices had acceptable signal intensity (≤ 40% drop) using the cross-flow nebulizer.

CHART 2 – *Cross-Flow high TDS response*

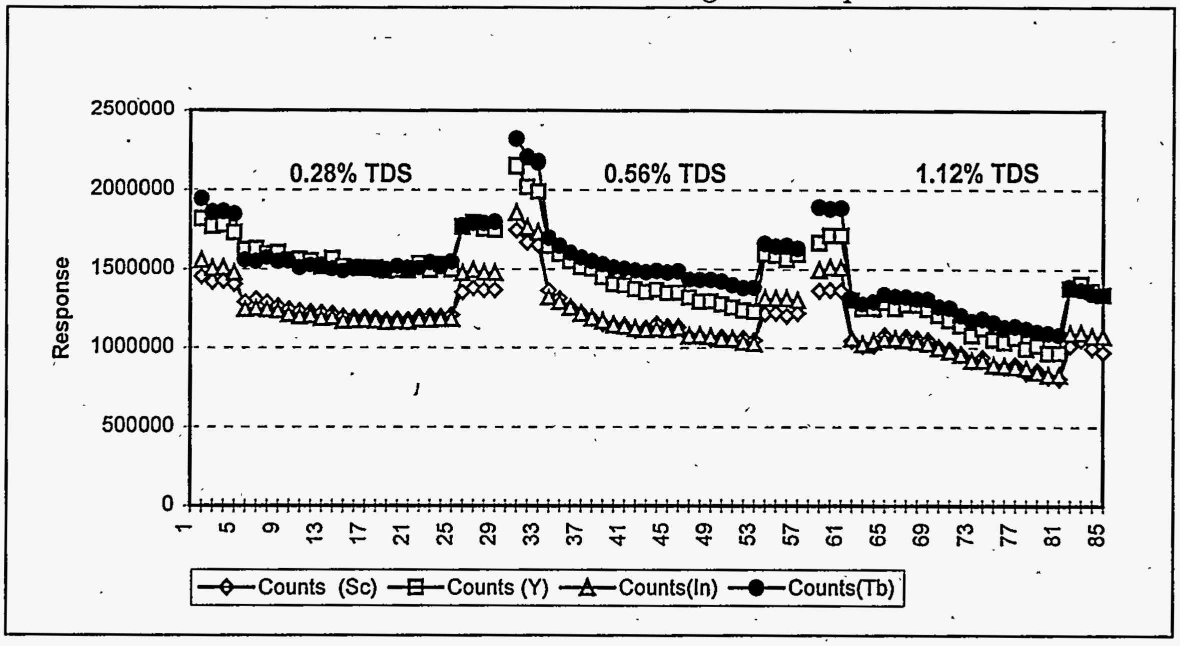


TABLE 4 - *Cross-Flow data summary for Tb*

Data Summary	Tb, 0.28% TDS	Tb, 0.56% TDS	Tb, 1.12% TDS
Average	1523650	1496159	1218408
STD @95% CL	52064	178580	186900
RSD @95% CL	3.42%	11.94%	15.34%
% Signal Drop	-16.8%	-21.0%	-23.1%

Micro-Concentric Nebulizer

The micro-concentric nebulizer model MCN-100 made by CETAC, is similar to the meinhard concentric nebulizer except that the diameter of the capillary and gap for the Ar carrier gas are smaller. The unique characteristics of the MCN-100 are a low sample uptake rate of about 20 µL/min and high efficiency. Higher Ar gas pressure and the design of the nebulizer tip may help prevent salt deposition (5). The peristaltic pump tubing supplied by CETAC with the MCN is made of PVC with a 0.19 mm ID. For ease of assembly and use, PVC tubing with a 0.25 mm ID was substituted. The PVC pump-tubing tends to elongate during the increased rpm for the rinse cycle and then relax to normal length during pump stabilization and analysis after pump speed is reduced. To facilitate using the increased pump speed for shorter rinse out times, the pump tubing was stretched to the longest stops on the pump head to minimize variations in length. The stretching and subsequent shrinking of the pump tubing also varies the internal diameter and resulting sample flow rate. This may contribute to some of the variability of the MCN technique. Using a longer rinse time (X5) and constant pump speed could possibly improve the precision of the results summarized below. Chart 3 shows the signal responses for analysis of 0.28%, 0.56%, & 1.12% TDS salt matrices; each bracketed by analyses of the control standard. The first three analysis sets were performed on the same day. The last run of 1.12% TDS salt matrix was analyzed on the next day to confirm the signal drop off of both salt and final control standard. Twenty replicate analyses were performed for each salt matrix. Only the 0.28% TDS matrix exhibited ≤ 40% signal drop using the MCN.

CHART 3 - *Micro-Concentric high TDS response*

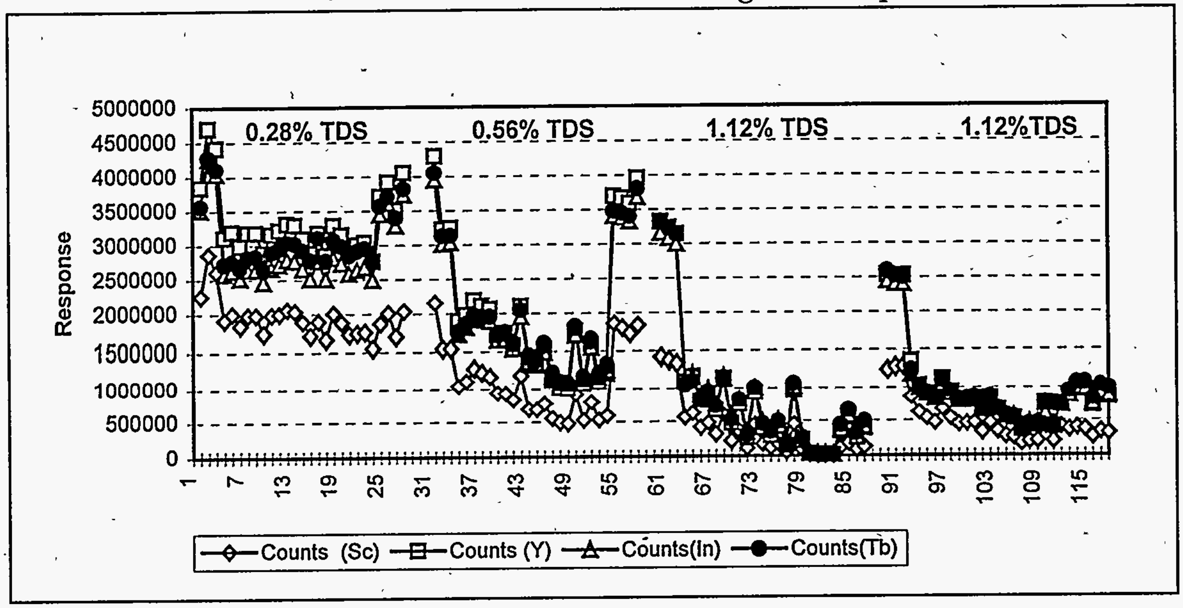


Table 5- *Micro-Concentric neb. analyses for Tb*
**[Note: % signal drop for Tb in 1.12% TDS based on 3 initial control standard analyses prior to salt matrix]*

Data Summary	Tb, 0.28% TDS	Tb, 0.56% TDS	Tb, 1.12% TDS	Tb, 1.12% TDS
Average	2873803	1580803	568979	762730
STD @95% CL	279949	655497	858546	492909
RSD @95% CL	9.74%	41.47%	150.9%	64.62%
% Signal Drop	-23.9%	-54.8%	-82.4%*	-70.0%*

V-Groove Nebulizer

The VGN used was that supplied with the HP 4500 instrument. Chart 4 shows the signal responses for analysis of 0.28%, 0.56%, & 1.12% TDS salt matrices; each bracketed by analyses of control standard. In addition to Sc, Y, In, and Tb; the elements Th and U were also added at the 100 µg/L level. All analyses were performed on the same day. Twenty replicate analyses were performed for each salt matrix. The 0.28% and 0.56% TDS matrices exhibited ≤ 40% signal drop using the v-groove nebulizer.

CHART 4 – *V-Groove high TDS response*

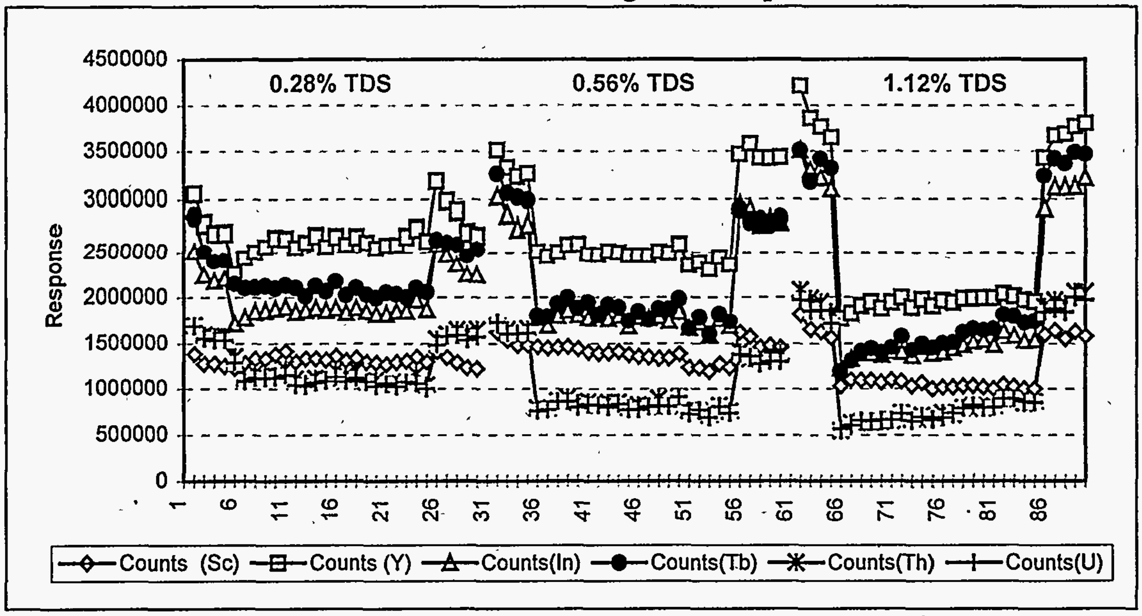


TABLE 6: *V-groove data summary for Tb & U*

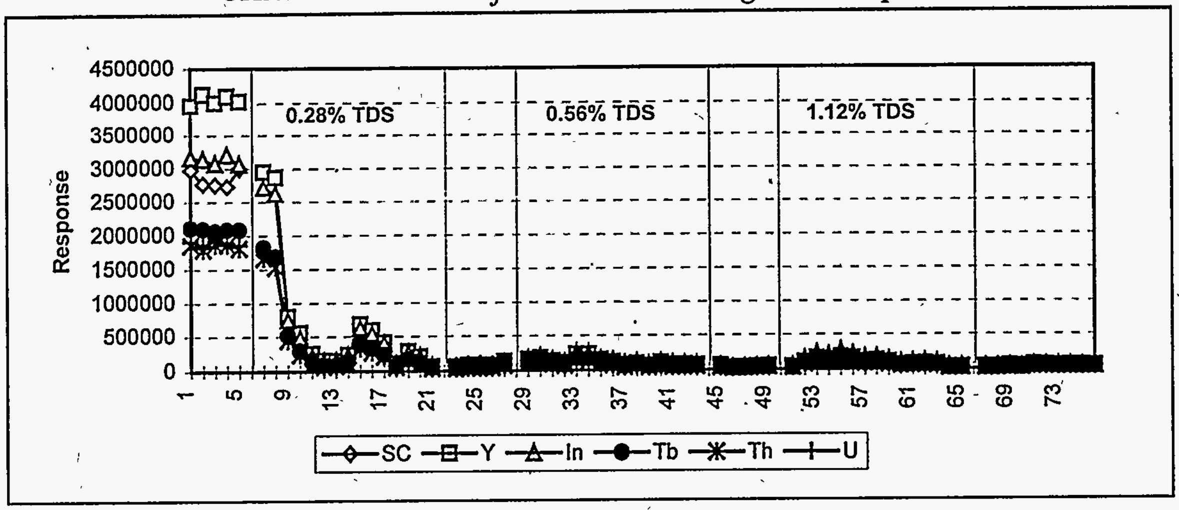
Data Summary	Tb, 0.28%	Tb, 0.56%	Tb, 1.12%	U, 0.28%	U, 0.56%	U, 1.12%
Average	2078037	1833196	1543179	1088016	795968	732833
STD @95% CL	107532	208048	345965	128789	106354	204329
RSD @95% CL	5.17%	11.35%	22.42%	11.84%	13.4%	27.88%
% Signal Drop	-18.6%	-37.6%	-54.3%	-30.4%	-45.6%	-61.0%

Direct Injection Nebulizer

The direct injection nebulizer (DIN) model Microneb 2000 is manufactured by CETAC. When using the DIN, the sample is delivered through a narrow inert capillary tube. Argon gas passes into the nebulizer tip through the narrow annular space between the sample capillary and the nebulizer tip. The result is a fine aerosol mist with a narrow particle size distribution. Due to the absence of large droplets, a spray chamber is not needed and the sample is directly injected into the central channel of the ICP. Because sample liquids must pass through a long narrow capillary, a sample injection valve is coupled with a high pressure gas displacement pump to deliver the sample to the nebulizer (6). In addition to control of gas flows and pressures, the DIN aerosol is optimized through extending or retracting the capillary tube relative to the nebulizer tip. This adjustment is under stepper motor control. One of the advertised advantages of the DIN include small sample sizes and quick rinse-outs between samples. This translates into improved efficiency of operations and reduced consumables (7) as well as waste reduction; both of which translate into potential cost savings. Application of the DIN for use in United States Department of Energy (DOE) and contractor laboratories to minimize analytical wastes from radioactive and/or hazardous samples has previously been proposed (8).

Chart 5 shows the signal responses for analyses of 0.28%, 0.56%, & 1.12% TDS salt matrices; each bracketed by analyses of control standard. All analyses were completed consecutively in one day. After the first 2 analyses of 0.28% TDS salt, the signal begins an abrupt drop. After 12 consecutive analyses of the 0.28% TDS salt, the response signal does not recover when switched back to analyzing the control standard.

CHART 5 – *Direct injection nebulizer high TDS response*



In attempting to regain instrument sensitivity, the sample and skimmer cones were replaced with new and the spectrometer and DIN re-tuned after running in the instrument for several hours. An apparent displacement of the capillary within the DIN proved to be the primary cause of the signal loss and was very sensitive and needed to be re-optimized each time the ICP was started. Although not represented here in a chart, the control and dilute salt matrix were again analyzed with the DIN. The analysis sequence was to analyze the control std. (5x) followed by repetitive analysis of a dilute salt matrix at 0.10% TDS. After the first 2 analyses of 0.10% TDS, the response dropped nearly to zero and remained low for the remainder of the 0.10% TDS. Further work with the DIN after these analyses gave further indication that it is extremely sensitive to the matrix TDS content. After a severe signal loss, the DIN could be re-tuned to regain sensitivity by adjusting the position of the capillary relative to the nebulizer tip and optimizing the vertical & horizontal torch positions. This was required frequently when running the dilute salt matrices

Conclusion:

For analysis of simulated radioactive high salt matrices > 0.2% TDS, the cross-flow is the nebulizer of choice in our laboratory at the parameters studied for both stability of response and to minimize matrix effect on signal loss/suppression. Chart 6 shows the compiled results of all the nebulizers studied normalized to an initial control standard response of 5 million counts for Tb. As in the previous charts, the dilute salts 0.28%, 0.56% and 1.12% are bracketed by control standard analyses. The MCN

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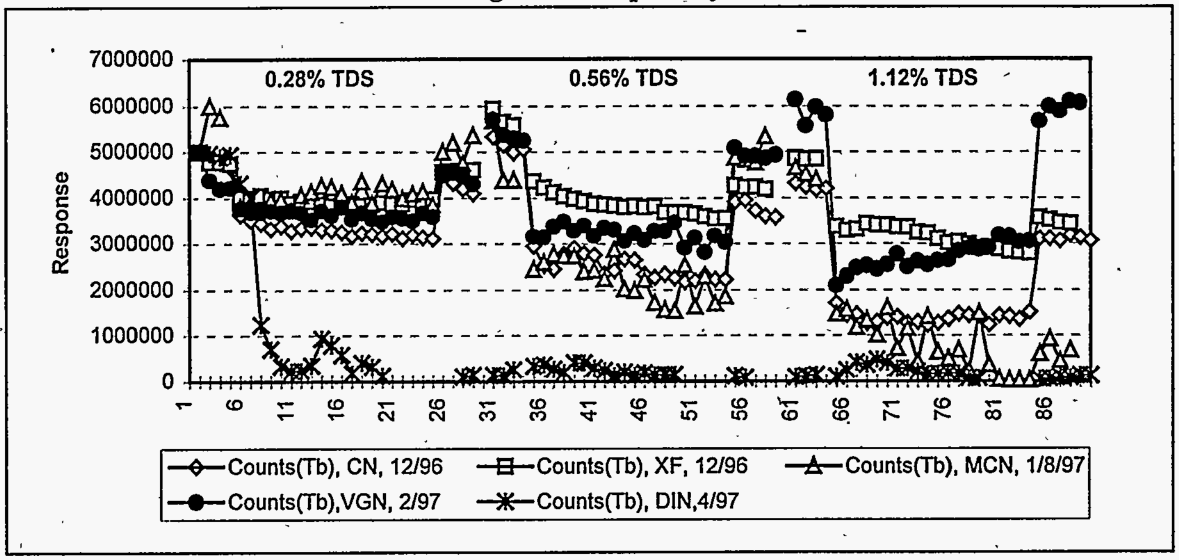
exhibited severe signal loss/suppression at 1.12% TDS, while the DIN is not recommended for high solids work.

CHART 6 – *Normalized high TDS response for all studied nebulizers*



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(5) HP 4500 Application Handbook; Section 1.2.2, revision 1.1, April 1996.

(6) Microneb 2000 direct injection nebulizer operator's manual, V5:060195, CETAC Technologies.

(7) CETAC Application Note: 001DIN1196U

(8) Crain, JS and Kiely, J.T., J. Anal. At. Spectrom., July 1996, Vol. 11, pp. 525-527.