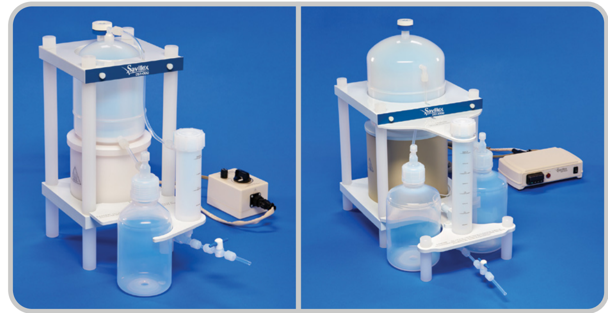
Savillex Technical Note

Performance of the DST-1000 and DST-4000 Acid Purification Systems

Overview



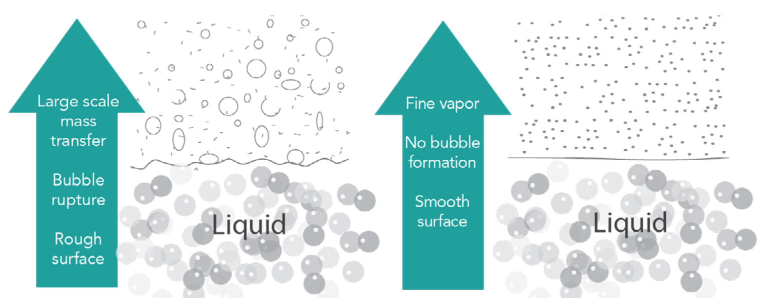
Savillex DST-1000 & DST-4000 Acid Purification Systems

Savillex's DST Acid Purification Systems are used by labs worldwide for the on-demand production of high purity acid for use with ICP-MS and other metals analysis techniques. This study examines the acid quality produced by the standard DST-1000 and fully automated DST-4000.

The ultra low detection limits of ICP-MS necessitate the use of high purity grade acids for the preparation of standards, sample dilutions and increasingly, even for sample digestion. Although commercially available bottled high purity (10 ppt) grade acid is readily available, it costs up to ten times more than trace metal (1 ppb) grade acid. Once opened, and during use, a bottle of high purity acid can easily become contaminated due to airborne contamination and/or analyst error. For these reasons, many labs are producing their own high purity acid using the Savillex DST range of acid purification systems. The DST range comprises of the DST-1000 standard system and the DST-4000 high throughput, fully automated system. Both systems convert trace metal grade acid into high purity grade acid using the principle of sub-boiling acid distillation.

Acid Purification by Sub-Boiling Distillation

Purification occurs via the process of sub-boiling distillation. Because the acid is never heated to boiling point, no bubbling, spitting, or splashing occurs. High purity acid vapor is produced, while metallic impurities in the acid feedstock remain in the liquid phase.



Extremely easy to use, the DST systems are integrated, compact units that fit in most fume hoods and require no cooling water. The systems feature a PFA vessel which acts as both an acid reservoir and a condenser, as shown in the schematic diagrams. The lower part of the vessel (reservoir) is surrounded by an electrically heated mantle, sealed inside a polymer bowl. Acid (trace metal grade) to be purified is added to the vessel via the fill tube which fills the reservoir from the bottom. The acid level in the reservoir is displayed by the liquid level gauge on the fill tube. The DST-1000 can process 1 L of acid at a time and the DST-4000 can process 4 L. Power is supplied

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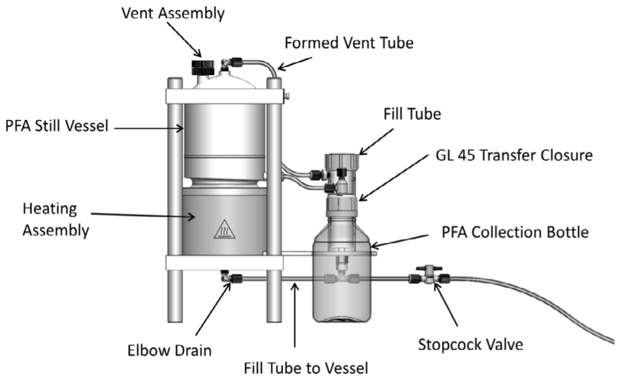
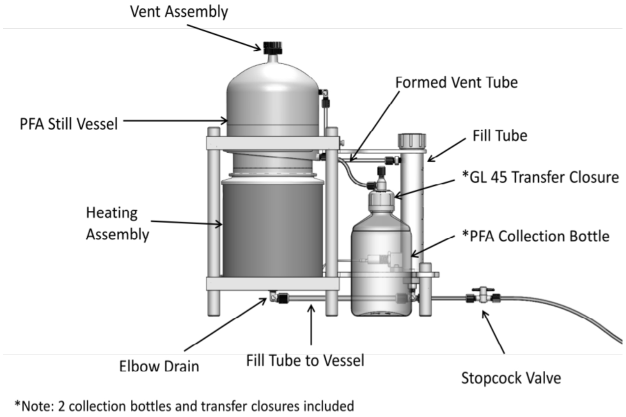
to the heater, and the acid in the reservoir is gently heated and high purity acid vapor is generated. The acid vapor condenses on the walls of the upper part of the vessel (condenser), collects in a channel running along the lower part of the vessel, and exits the system via a PFA tube into a Purillex™ PFA collection bottle (a 1 L bottle for DST-1000, and two 2 L bottles for the DST-4000). The size and shape of the vessel promotes efficient condensation of acid which eliminates the need for water cooling.



DST-1000



DST-4000

A controller maintains the required temperature used for heating the acid. The DST-1000 has a basic temperature controller with three temperature settings. The DST-4000 has a digital variable temperature controller which can be programmed to heat the acid between 40-95˚C. In addition, the DST-4000 is equipped with a liquid level sensor that will automatically shut off the heat to the DST-4000 when the liquid level in the reservoir drops below 500 mL. Operation is very simple: add acid and switch on the power to start generating high purity acid. The auto shut-off feature on the DST-4000 means the operator never needs to check on the acid level. For both systems, the temperature settings only affect the production rate and not the purity of the acid. The maximum acid temperature that can be generated by the heating element is below the boiling point of any of the acids that can be purified, preventing metal contaminants from being carried over to the distillate.

The vent assembly on the top of the vessel and the vent in the collection bottle transfer closure allow air into the vessel as the acid is distilled, and allow displaced air out of the bottle as it fills. All vent ports are fitted with PTFE membranes, which prevent airborne contamination from entering the system. The vent tube on each unit maintains even pressure throughout the system as it is filled and drained. Aside from the PTFE vent membranes, all wetted parts are PFA. At the end of the run, residual acid, containing the metal contaminants in the initial feedstock, is drained to waste.

Note: The actual concentration of acid may change between feed acid and distilled acid. When distilling commercially available concentrated HNO_3, the concentration in the distilled acid will be essentially unchanged from the feed acid. This is because the concentration of the feed acid is very close to the azeotropic concentration (65-70% w/w). In the case of HCl and HF, the azeotrope concentration is lower than the concentration of commercially available acid, which means that the feed and distilled acid concentrations will be different.
The simplest way to avoid this is to dilute the feed acid to match the azeotropic concentration – 20% w/w for HCl and 37% w/w for HF – then the distilled acid concentration will be unchanged from the feed acid. If a higher concentration of distilled acid is required, use undiluted feed acid and if necessary, measure the acid concentration after distillation.

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Performance of the DST-1000 and DST-4000 Acid Purification Systems

Model	Capacity (L)	Production (mL/hr)*	Auto Shut-Off?	Distilled Acid Quality (ppt)
DST-1000	1	38	No	<10
DST-4000	4	82	Yes	<10

*Average combined hourly production rate of HF, HCl, and HNO_3.

DST-1000 vs. DST-4000

The table above compares the specifications and performance of the DST-1000 and DST-4000. The DST-1000 can produce 500 mL of high purity acid (HNO_3, HCl, or HF) in approximately 12 hours, while the DST-4000 can produce 1 L of high purity acid in the same time period.

Acid Quality

The quality of HNO_3, HCl, and HF produced by the DST was evaluated by a semiconductor lab. Following an initial cleaning protocol, trace metal grade acid was processed in a DST-1000, operated in the HI setting (fastest distillation rate) and collected. A single distillation was performed (i.e. the acid was not double distilled). Replicate samples were preconcentrated using an in-house preconcentration system, along with replicates of a new bottle of commercial high purity HNO_3, opened immediately prior to use, and trace metal grade HNO_3. All sample prep was performed in a Class 1 cleanroom. A blank and spike recovery were also prepared with each replicate. The samples were then analyzed using Agilent 7500cs and 8800 ICP-MS. Table 1 shows the detection limits reported using the preconcentration technique, and analytical data for commercial high purity (10 ppt) grade HNO_3 and the DST-produced HNO_3. The DST-produced acid was found to be equivalent in quality to the commercial high purity grade – even though the commercial acid bottle was opened for the first time.

Analyte	Detection Limit	High Purity Grade HNO_3 (10 ppt Grade)	DST-Produced HNO_3
Li	1	<1	<1
Na	1	1	<1
Mg	1	2	<1
Al	1	1	<1
K	1	<1	<1
Ca	1	<1	<1
Cr	1	5	1
Fe	1	7	4
Ni	1	7	1
Cu	1	6	4
Zn	1	<1	<1
W	1	<1	<1
Hf	1	<1	<1
Mn	1	<1	<1
Ti	1	<1	<1
Co	1	<1	<1
Ge	1	<1	<1
Sb	1	<1	<1
Te	1	<1	<1
Ag	1	<1	<1
Au	1	<1	<1
Gd	1	<1	<1
La	1	<1	<1
Pt	1	<1	<1
Sr	1	<1	<1
Zr	1	<1	<1
In	1	<1	<1
Mo	1	2	<1
Ta	1	<1	<1
Be	1	<1	<1
V	1	1	1
As	1	2	2
Cd	1	<1	<1
Cs	1	<1	<1
Ba	1	<1	<1
Pb	1	<1	<1

Table 1: Comparison of trace metal content in commercial high purity HNO_3 with DST produced HNO_3, using the DST-1000. DST-produced HNO_3 was obtained by a single distillation from trace metal grade (1 ppb). All data is in ppt, and was generated by a semiconductor lab evaluating the DST (lab name withheld by request).

An analysis was also performed on bottled commercial high purity HCl, comparing metal content with. DST-produced HCl using the same conditions and procedure as with HNO3. Once again, for many elements, the DST-produced acid is cleaner than commercial high purity grade – even though the commercial acid bottle was opened for the first time. DST-produced acid was measurably lower in Ni, Ti, and As. Hg was also measured to assess the suitability of DST-produced acid for cold vapor AA. As can be seen, the DST-1000 is able to remove Hg from HCl, making it well suited for cold vapor AA use.

Analyte	Detection Limit	High Purity Grade HCl (10 ppt Grade)	DST-Produced HCl
Li	1	<1	<1
Na	1	<1	7
Mg	1	<1	<1
Al	1	1	6
K	1	<1	2
Ca	1	2	4
Cr	1	5	3
Fe	1	20	17
Ni	1	29	2
Cu	1	1	4
Zn	1	7	1
W	1	<1	<1
Hf	1	<1	<1
Mn	1	<1	<1
Ti	1	130	1
Co	1	11	<1
Te	1	<1	<1
Ag	1	<1	<1
Au	1	<1	<1
Gd	1	<1	<1
La	1	<1	<1
Pt	1	<1	<1
Sr	1	<1	<1
Zr	1	<1	<1
In	1	<1	<1
Mo	1	1	2
Ta	1	<1	<1
Be	1	<1	<1
V	1	<1	<1
As	1	37	6
Cd	1	<1	<1
Cs	1	<1	<1
Ba	1	<1	<1
Pb	1	<1	<1
Hg	1	1	<1

Table 2: Comparison of trace metal content in commercial high purity HCl with DST-produced HCl, using the DST-1000. DST-produced HCl was obtained by a single distillation from trace metal grade (1 ppb). All data is in ppt, and was generated by a semiconductor lab evaluating the DST (lab name withheld by request).

Finally, an analysis was also performed on bottled commercial high purity HF with DST-produced HF, using the same conditions and procedure as with HNO_3. As can be seen, the DST-produced acid is equivalent in metal content to commercial high purity grade – even though the commercial acid bottle was opened for the first time.

Analyte	Detection Limit	High Purity Grade HF (10 ppt Grade)	DST-Produced HF
Li	1	<1	<1
Na	1	<1	6
Mg	1	2	<1
Al	1	8	6
K	1	3	3
Ca	1	9	2
Cr	1	1	3
Fe	1	1	9
Ni	1	<1	1
Cu	1	<1	2
Zn	1	2	3
W	1	<1	2
Mo		3	1
Ti	1	<1	6
Co	1	<1	<1
Ge	1	<1	<1
Sb	1	<1	<1
Rh	1	<1	<1
Rh	1	<1	<1
Be	1	<1	<1
V	1	<1	<1
Mn	1	<1	<1
Zr	1	<1	<1
Ag	1	<1	<1
Cd	1	<1	<1
Sn	1	<1	<1
Cs	1	<1	<1
Ba	1	<1	<1
Hf	1	<1	<1
Ta	1	<1	<1
Pb	1	<1	<1

Table 3: Comparison of trace metal content in commercial high purity HF with DST-produced HF, using the DST-1000. DST-produced HF was obtained by a single distillation from trace metal grade (1 ppb). All data is in ppt, and was generated by a semiconductor lab evaluating the DST (lab name withheld by request).

Acid Quality Comparison – Typical Geochemical Elements

DST systems are used widely in geochemistry since very high purity acid is required, and since geochemistry labs use large amounts of high purity acid for sample prep – both for sample digestion and with column chemistry. Although most of the traditional elements studied in geochemistry (Pb, U, Th, REEs and others) are "easy" to measure by ICP-MS and TIMS due to their relative rarity in nature and freedom from interferences (in ICP-MS), the measurement levels required are incredibly low.

Prof. Stein Jacobsen at Harvard University has several DST-1000s and a DST-4000. He compared acid quality produced by both systems for traditional geochemistry elements. The acid samples (blanks) were measured with a quadrupole ICP mass spectrometer (ICP-QMS). For comparison, results are given for concentrated HCl acid produced in the time period between 1983 and 2008 from compressed HCl gas (CG). The gas was scrubbed in a system made from Savillex PFA parts and then reacted with ultrapure water in a 5 L PFA bottle. The CG HCl blanks for Rb, Sr, Nd, and Sm were measured by isotope dilution thermal ionization mass spectrometry (TIMS).

According to Prof. Stein Jacobsen, University of Harvard:

"Detection limits are better by TIMS and so lower values by this method does not mean that there is any actual difference between the true blank level for Nd and Sm for the CG acid compared to the DST acid. Note that we have found that the commercially available trace metal grade acid is not always as good as the vendor claims that it is. The values above are for distillation of the BDH trace metal grade acids (ppb grade) which we have found to have blanks consistent with their specifications. When the stills were new they produced lower quality acids but we did not monitor this in detail. It took about five distillations to get rid of most of this initial contamination in the stills."

It can be seen from the data that the DST-1000 and DST-4000 produce equivalent quality acid for geochemical elements. It also demonstrates, when operated with good technique, the incredible sensitivity of modern ICP-QMS for un-interfered elements that are not common in nature.

	DST-1000	DST-1000	DST-1000	DST-4000	Compressed HCl Gas
	DIW	16N HNO_3	12N HCl	12N HCl	12N HCl
	ICP-QMS	ICP-QMS	ICP-QMS	ICP-QMS	TIMS
Element	ppt	ppt	ppt	ppt	ppt
Rb	<0.08	<0.5	<0.2	<0.2	<0.2
Sr	<0.03	<0.6	<0.2	<0.2	<0.2
Ru	<0.01	<0.5	<0.2	<0.004	
Rh	<0.003	<0.2	<0.06	<0.002	
Pd	<0.03	<0.03	<0.03	<0.002	
Ba	<0.2	<2	<0.3	<0.3	
Nd	<0.01	<0.2	<0.05	<0.01	<0.0001
Sm	<0.0005	<0.0005	<0.0005	<0.0005	<0.0001
Gd	<0.0005	<0.03	<0.0005	<0.0005	
Lu	<0.0005	<0.0005	<0.0005	<0.0005	
Hf	<0.001	<2	<0.3	<0.008	
W	<1	<3	<3	<0.9	
Ir	<0.0001	<0.001	<0.0001	<0.0001	
Pt	<0.001	<0.002	<0.001	<0.001	
Au	<0.001	<0.05	<0.01	<0.0005	
Pb	<0.2	<0.6	<0.5	<0.5	
Th	<0.0009	<0.08	<0.03	<0.008	
U	<0.002	<0.002	<0.01	<0.002	

Table 4: Comparison of acid quality produced by DST-1000, DST-4000 and HCl produced from compressed gas. DSTs were operated at fastest distillation rate. Data courtesy of Prof. Stein Jacobsen, Harvard University, USA.

Summary

The DST systems have been shown to produce very high quality acid, at a fraction of the cost of commercially available high purity grade acid, enabling the use of high purity acid not only for standard preparation, but even for sample prep and cleaning. In addition, the DSTs produce fresh, high purity acid on demand, and so the degradation in quality over time with commercial high purity acid (as the bottle is repeatedly opened) is avoided.

Click here to learn more about the DST-1000 & DST-4000 and buy online.

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