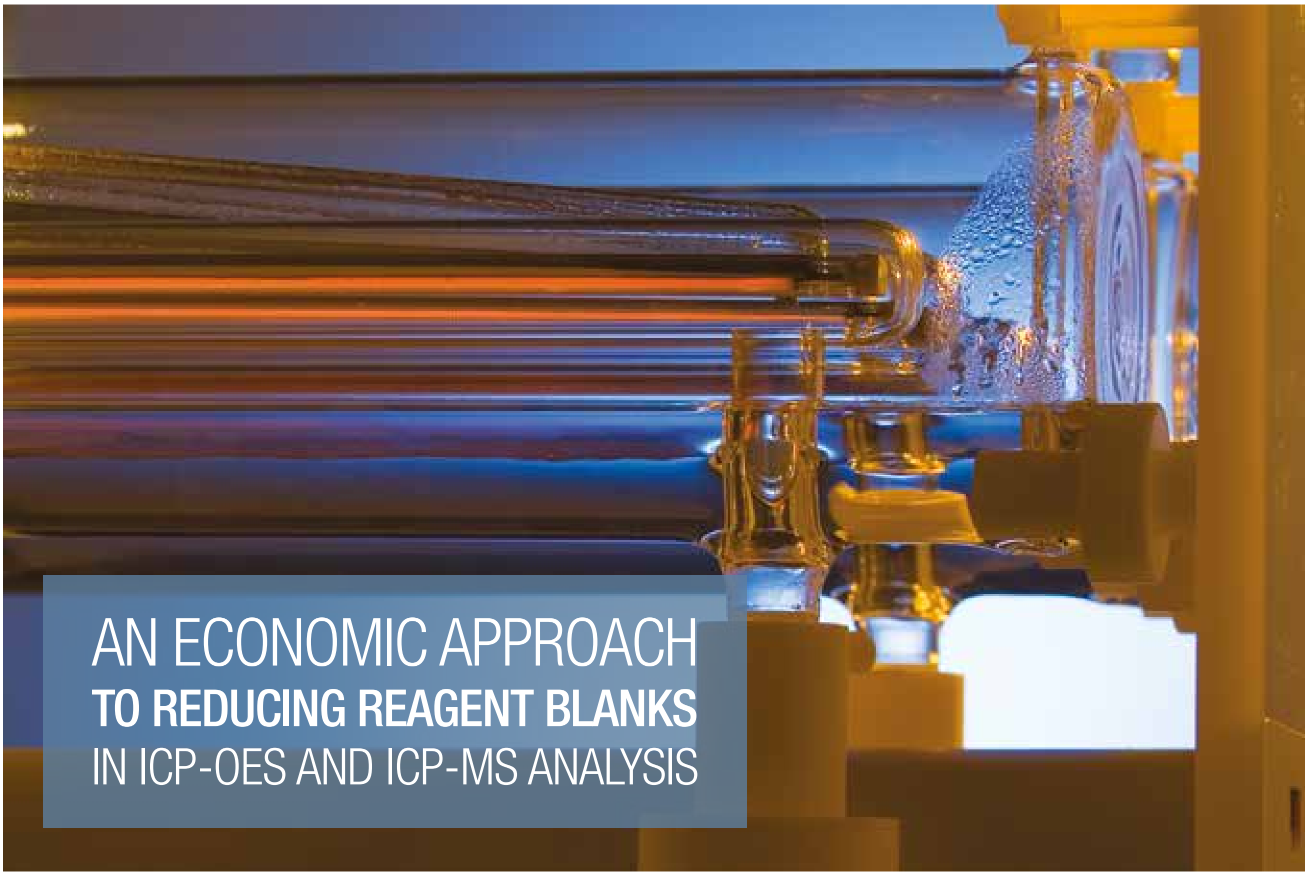

AN ECONOMIC APPROACH **TO REDUCING REAGENT BLANKS** IN ICP-OES AND ICP-MS ANALYSIS

duoPUR Acid Purification System allows laboratories to purify low-cost reagent grade acids.

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The increasing demand for lower detection limits is a major consideration for any laboratory that is carrying out elemental determinations by ICP-OES and ICP-MS. The analytical instrument is just one component in achieving the lowest limits of detection. The other critical area that puts significant demands on a laboratory's overall detection capability is to ensure that the sample preparation procedure does not contribute any additional sources of contamination. Several factors must be considered when looking to minimize contamination and reduce blank levels when preparing samples for analysis by plasma spectrochemistry. These include equipment cleanliness, reagent purity, quality of materials, and the digestion procedure itself.

REAGENT PURITY

Currently, many laboratories purchase expensive high-purity acids for trace elemental analysis. There is, however, an alternative approach. Milestone has developed the duoPUR, a sub-boiling distillation system that allows laboratories to make their own high-purity acids at dramatically reduced costs. The advantages of the duoPUR include:

- Up to 90% cost savings by purifying low-cost reagent grade acids

- High productivity of up to 3 liters in eight hours
- Continuous supply of high-purity acids
- On-demand acid purification
- Re-purification of contaminated acids
- Single or double distillation

PRINCIPLE OF OPERATION

Sub-boiling distillation is a technique based upon vaporizing a liquid by radiative heating of its surface to prevent boiling. It is recognized as the best method to obtain high-purity reagents typically used in ultra-trace analysis. In conventional distillation, violent boiling action generates aerosolized particles, resulting in re-contamination of the distillate by the original liquid. Surface evaporation during sub-boiling distillation prevents this, yielding a higher purity distillate (Figure 1).

The duoPUR (Figure 2) consists of two high-purity quartz distillation units with two heating elements (1), a water-cooled condenser (2), reagent collection bottle (3), and a drain. The distillation process is microprocessor controlled, allowing the user to set the distillation time and power level. Infrared heating gently vaporizes the surface liquid, accelerating evaporation, and preventing aerosolized particles. Vaporized liquid is collected on an inclined cold finger where it condenses and drips into the high purity PFA collection bottle.

By using higher power, faster distillation rates are achieved, but at the sacrifice of purity. Therefore, simple method development will determine the optimum program time for the required acid purity. Table 1 shows typical distillation rates for water, nitric and hydrochloric acids in mL/hour, based on varying infrared power settings.

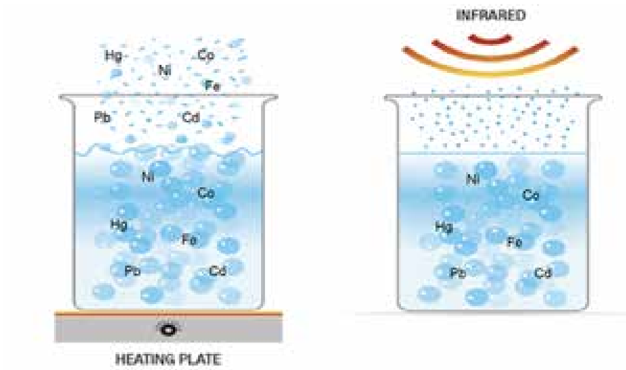

Figure 1: Conventional heating compared to sub-boiling infrared heating.

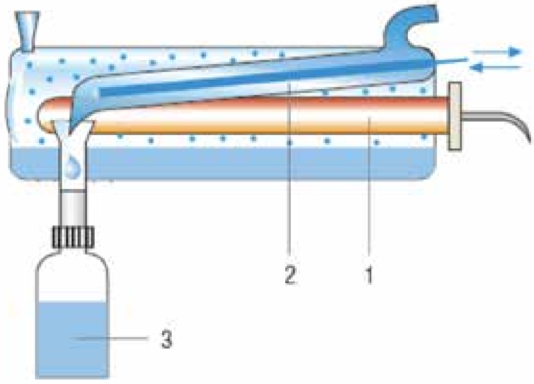

Figure 2: duoPUR acid purification system.

Infrared power (W)	Productivity (mL/hour)		
	HNO_3	HCl	H_2O
200	50	45	65
400	145	155	175
600	235	260	270
800	325	375	360
1,000	420	445	450

Table 1: duoPUR typical distillation rates for HNO_3, HCl, H_2O in mL/hour based on varying infrared power settings

PURIFICATION PERFORMANCE

The capability of the duoPUR system is shown in Table 2, which compares trace element results from a laboratory carrying out the double-distillation of reagent-grade nitric acid with that of Ultrex II nitric acid from J.T. Baker. It can be clearly seen that for most elements, duoPUR data shows comparable results to the ultra-high purity acid.

	duoPUR Double-Distillation Reagent-Grade Nitric Acid	Baker **Ultrex® II** High-Purity Grade Nitric Acid
Element	Concentration (ppt)	Concentration (ppt)
Ag	16	<10
Al	<10	<20
As	19	<20
Ba	<10	<10
Ca	<10	<10
Cd	<50	<10
Co	<10	<10
Cr	<10	<10
Cu	<10	<10
Fe	<10	<10
Mg	<10	<10
Mn	12	<10
Mo	22	<10
Ni	<10	<20
Pb	31	<10
Sb	18	<10
Sn	11	<20
Ti	<50	<20
V	<10	<10
Zn	<10	<10

Table 2: Comparison of contamination levels of double distilled HNO_3 using the duoPUR with that of Ultrex II (J.T. Baker) ultra-high purity nitric acid

SUBCLEAN SYSTEM

The subCLEAN is a compact system that uses sub-boiling distillation with forced air cooling where all parts in contact with acid are made of high purity PTFE instead of quartz, making it suitable for use with HF, as well as HNO_3 and HCl. In addition, if a double distillation is carried out, the purity of the acid is significantly increased as exemplified by the data for reagent-grade nitric acid in Table 3.

	subCLEAN Single-Distillation Reagent-Grade Nitric Acid	subCLEAN Double-Distillation Reagent-Grade Nitric Acid
Element	Concentration (ppt)	Concentration (ppt)
Ag	<46	<1.5
Al	<557	<147
As	<3	<0.9
Ba	<25	<3.5
Ca	<900	<157
Cd	<8.1	<1.8
Co	<6	<1
Cr	<118	<4.6
Cu	<58	<21
Fe	<1000	<210
Mg	<195	<42
Mn	<9.7	<2.1
Mo	<7.1	<0.4
Ni	<155	<23
Pb	<10	<2.5
Sb	<6.1	<0.5
Sn	<22	<9.1
Ti	<59	<8.1
V	<51	<11
Zn	<261	<49

Table 3: Comparison of purity between single and double distillation of reagent grade nitric acid using the subCLEAN

COST SAVINGS

It's also worth pointing out that there are significant cost savings when using the duoPUR or the subCLEAN, compared to purchasing high purity reagents. This is demonstrated in the following example (all costs are provided as estimates for example purposes only): If a laboratory processes 200 samples per month using 30 mL of ultra-pure nitric acid (J.T. Baker Ultrex II) per sample, it will use 6 L of ultra-pure acid at a cost of approximately $5,500 per month or $920 per liter per month. Six liters of reagent-grade acid (Sigma Aldrich) would only cost approximately $250 per month, or $40 per liter per month. By distilling this lower grade acid, $5,300 would be saved every month, which translates to the duoPUR paying for itself in less than four months. This is demonstrated in Table 4, which shows the cost saving for both nitric and hydrochloric acid.

By using the simple calculation shown in Figure 3, the cost savings for your lab can be estimated. Simply fill in your own information to calculate the potential monthly savings.

Mineral Acid	Ultra Pure Grade per Liter (J.T. Baker Ultrex II)	Reagent Grade per Liter (Sigma Aldrich)
Nitric Acid	$920	$40
Hydrochloric Acid	$890	$40

Table 4: Approximate costs per liter of ultra-pure nitric and hydrochloric acids (J.T. Baker Ultrex II) compared to producing it from reagent-grade acids (Sigma Aldrich) using the duoPUR sub boiling distillation system

Average Liters of Ultra Pure Acids you use per month		X cost per L		=	BOX A
Same Number of Liters **but now using Reagent Grade Acid		X cost per L		=	BOX B =
		Subtract Box B from Box A to tell you how much you will save per month on acid			BOX C

Figure 3: Simple calculation to estimate cost savings per month using the duoPUR. Note: This worksheet should only be taken as an approximation of cost savings.

CERTIFIED QUALITY

Ultra-pure reagents are supplied with a certificate to attest the quality. However, once the bottle is opened, the contaminant levels can change rapidly. Analysts may adversely affect the quality of reagents through daily, repeated handling, especially in high throughput labs. The potential impact of repeated handling can be observed by looking at the effect on four different bottles of ultrapure water in a typical eight-hour workday. The initial sum total metal contamination for 10 common elements was around 74 ng/L. After eight hours of repeated handling by an analyst, contaminant levels rose to a range of 368–2,627 ng/L across the four bottles tested, a 5- to 25-fold increase (Table 5).

On-demand reagent purification with sub-boiling systems supplies fresh, high-purity reagents in accordance with laboratory requirements and allows for re-purification of contaminated acids. By validating the sub-boiling process, any laboratory can certify the quality of acid produced. Method optimization is done by performing purifications at different conditions, followed by ICP-MS analysis to check contaminant levels. Once the method has been optimized to achieve the desired grade of purity, the ICP-MS analysis verifies the acid quality obtained with the sub-boiling system.

"Method optimization is done by performing purifications at different conditions, followed by ICP-MS analysis to check contaminant levels."

Element	Reference Bottle Freshly Prepared	Range of four bottles used for routine preparation operations over 8-hr day
Al	11	40–120
Ca	20	100–700
Cr	0.3	0.4–2
Cu	2	2–12
Fe	4	5–60
K	20	100–300
Mg	2	9–70
Na	10	100–1300
Ti	0.2	0.3–13
Zn	4	11–50

Table 5: Influence of analyst handling on ultrapure water contamination levels Think Blank Clean Chemistry Tools for Atomic Spectroscopy, R.C. Richter - J.A. Nóbrega - C. Pirola, 2016, Milestone Srl

CONCLUSION

High-purity acids and reagents are critical to controlling the analytical blank, the "Achilles heel" of trace analysis, and to improving ICP-OES and ICP-MS detection limits. Reagent purity, cleanliness of the materials used in sample preparation, the laboratory environment, and the skill of the analyst are all factors that contribute to contamination. The duoPUR and subCLEAN systems offer a truly cost-effective way of cleaning reagent grade acids and avoiding the expense of purchasing the highest purity acids.

ABOUT MILESTONE

With over 50 patents and more than 20,000 instruments installed in laboratories around the world, Milestone has been widely recognized as the global leader in metals prep technology for the past 30 years. Committed to providing safe, reliable and flexible platforms to enhance your lab's productivity, customers worldwide look to Milestone for their metals digestion, organic extractions, mercury analysis and clean chemistry processing needs.

Robert Thomas is the principal of Scientific Solutions, a consulting company that serves the application and writing needs of the trace element user community. He has worked in the field of atomic and mass spectroscopy for more than 40 years and has written over 90 technical publications including a 15-part tutorial series on ICP-MS. He recently completed his fourth textbook entitled **Measuring Elemental Impurities in Pharmaceuticals**: A Practical Guide. He has an advanced degree in analytical chemistry from the University of Wales, UK, and is also a Fellow of the Royal Society of Chemistry and a Chartered Chemist. He has led the heavy metals, plasma spectrochemistry task force on the ACS Committee on Analytical Reagents.

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