Spectroscopy

On-Demand Production of High-Purity Acids in the Analytical Laboratory

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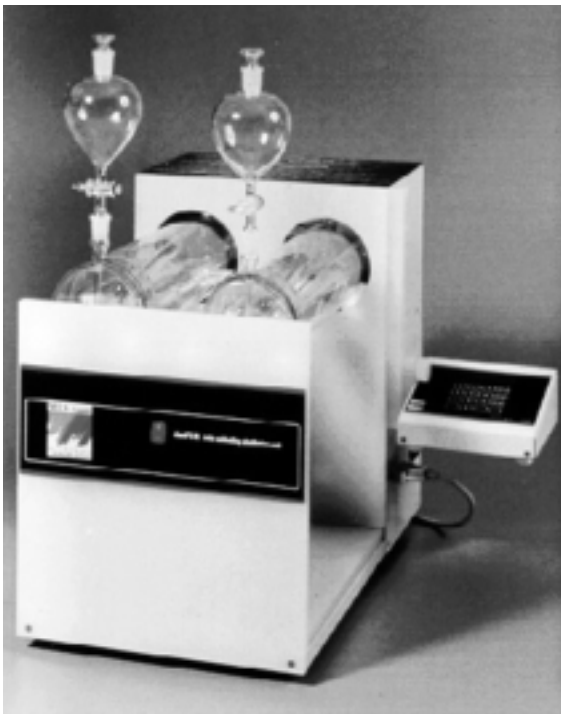

On-Demand Production of High-Purity Acids in the Analytical Laboratory

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Analytical chemists are increasingly being required to analyze samples having trace metal concentrations in the 10-6–10-9 g/g range for solids and the 10-9–10-12 g/g range for solutions and suspensions. These multielement analyses are normally done using inductively coupled plasma mass spectrometry (ICP–MS) or inductively coupled plasma atomic emission spectrometry (ICP–AES); however, these instruments require a homogeneous sample solution because they compare atomic relationships — for example, mass-to-charge ratio or wavelength energy intensity — on an atomic level with time integration. Sample homogeneity for solids, solutions, and suspensions is typically achieved through mineral acid dissolution.

Mineral acid dissolution procedures require from 10 mL of acid, for closed-vessel microwave methods, to 100 mL of acid for open-vessel methods, to be added to the sample with heating to achieve dissolution. Acids used for dissolution contain variable levels of trace metal impurities, which can make a significant contribution to the method's analytical blank. The analytical blank, not the sensitivity of the instrument, determines the detection limit. Thus, to measure an analyte with a final solution concentration of 1 ng/mL, the acid used for dissolution must have a contamination level <500 pg/mL for a soil digested with 20 mL of acid and <100 pg/mL for an aqueous solution or suspension digested with 5 mL of acid.

These high-purity acids must be purchased or produced in the laboratory. The purchasing of high-purity acids makes sense when only a small amount is needed to process samples on a nonroutine basis. Purchasing is also a good idea when production is difficult, time consuming, or safety concerns exist, such as when using hydrofluoric acid; however, when significant quantities (250–1000 mL/day) of acid are needed or budgetary concerns limit high-purity acid purchases, as in a university laboratory, then in-lab production is the logical choice.

We have been experimenting with a commercially available acid distillation system to produce high-purity acids here in the Center for Microwave and Analytical Chemistry (CMAC) at Duquesne University. This system is capable of producing high-purity nitric, hydrochloric, sulfuric, and perchloric (with appropriate safety procedures) acids and water. This article outlines our experience and successful use of this system to produce high-purity nitric acid that is comparable to commercially available high-purity acids at a fraction of the cost.

INSTRUMENTATION

Acid-purification system. We used a first-generation prototype unit of the duoPUR Sub-boiling distillation system (Milestone Inc., Monroe, CT) to prepare the acids for this study. This system consists of two high-purity quartz distillation units. Each unit contains two infrared heating elements that supply a maximum power of 1250 W, a water-cooled condenser, reagent addition and collection bottles, and a drain. The distillation process is microprocessor controlled, allowing users to set distillation and cooling times and power level (Figure 1). The still is housed in a class 100 exhausted clean air hood (Figure 2).

Acid-purity analysis. Microwave evaporation was carried out in an Ethos 1600 Microwave Labstation (Milestone Inc.) using a custom-built rotor. An HP-4500 ICP-MS (Agilent Technologies, Wilmington, DE), in standard configuration, equipped with a quartz Meinhard concentric nebulizer and a class 10 clean hood for the sample introduction system, was used for analysis. Both the microwave unit and ICP-MS systems are located in a multispace clean room facility.

METHODS

Acid production. We produced 2 L of single-distilled nitric acid from Fisher ACS Plus grade nitric acid (Fisher Scientific). We stored 500 mL of the single-distilled nitric acid in an acid-

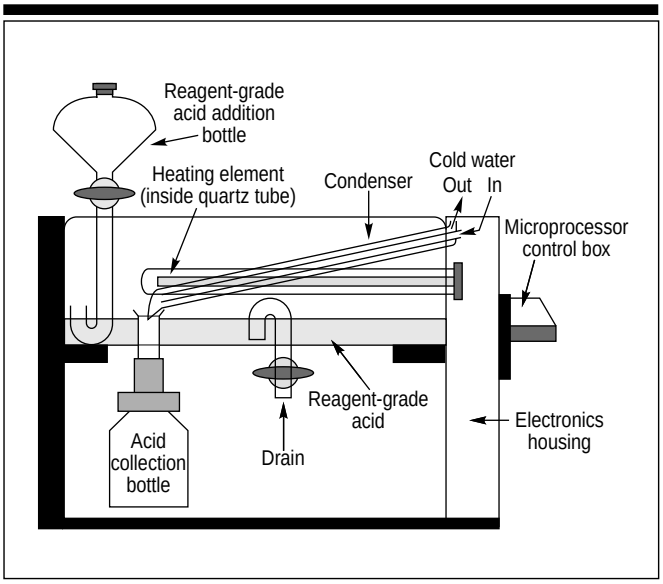

Figure 1. Schematic of the subboiling distillation system. Second heating element not shown for clarity purposes.

cleaned PTFE bottle for analysis. The remaining 1.5 L of single-distilled nitric acid was used to produce 500 mL of double-distilled nitric acid. We cleaned the still between distillations by first draining the remaining reagent-grade acid and rinsing several times with 500 mL of 18-MΩ water. Both grades of nitric acid were produced in a single distillation unit running for 6 h/day at 70% power with the condenser cooled to 10 °C.

Acid-purity analysis. We took 50 g of either single- or double-distilled nitric acid and placed it in an acid-washed TFM PTFE microwave vessel. We then spiked the acid with 250 µl of internal standard solution and evaporated the acid–standard mixture to dryness in the microwave unit. We reconstituted the mixture to 5 g with 5% nitric acid prepared from distilled 18-MΩ water and the double-distilled nitric acid and analyzed the reconstituted mixture by ICP-MS. All sample handling and manipulation were performed in a class 10 clean hood in a class 100 cleanroom.

RESULTS AND DISCUSSION

Acid-purification process and conditions. No single purification process is capable of removing all impurities from acids. Sub-boiling distillation has been shown to be the method of choice for acid purification and was the process used in this study (1–4). In sub-boiling distillation, infrared heaters vaporize the surface liquid. The vaporized liquid is collected on an inclined water-cooled condenser and drips into the collection container (Figure 1). Vaporization without boiling is the key element of this purification process because it prevents aerosolized particles from depositing on the surface of the condenser. These aerosolized particles are the source of the physical contamination of the distillate in a boiling system. The high-purity acids produced in this manner have essentially the same concentration as the reagent-grade acids used to produce them (3, 4). High-purity nitric acid produced in this way will also contain varying amounts of dissolved nitrogen dioxide gas. The purification conditions used to produce the acid used in this study resulted in a significant amount of nitrogen dioxide gas being dissolved in the purified acid, giving the acid a yellow color, which, for most mineral acid dissolution procedures, does not cause any problems. In rare cases, where the dissolved nitrogen dioxide gas may interfere with an analysis, high-purity acid with a minimal amount of dissolved nitrogen dioxide can be produced by operating the still at a low power setting. In our laboratory, reducing the power decreased the volume of acid produced in 6 h from 500 mL to about 50 mL.

Having an efficient and high-purity still is only part of producing high-purity acids. Any material that comes in contact with the purified reagent may transfer contamination to it. Therefore the bottles used to collect and store the purified acid must be made of a high-purity material such as a fluoropolymer (PTFE-FEP) and thoroughly cleaned before use (5). Also, the acid-purification system is a closed system during production, but the system can become compromised when the reagent-grade acid is added or when the purified acid is being transferred from the collection bottle to storage and distribution bottles. Laboratory air that becomes trapped inside the still can deposit elemental contamination onto the condenser or collection bottle, affecting the quality of acid produced. This problem can be overcome by placing the still in a clean environment as we have done in our laboratory. Class 100 clean hoods are the best solution and can be purchased or built with plans downloaded from the clean chemistry section of our SamplePrep World Wide Web site (6). These units should have an adjustable exhaust rate to regulate the airflow, protect the still from laboratory contamination, and minimize the acid fumes in the room.

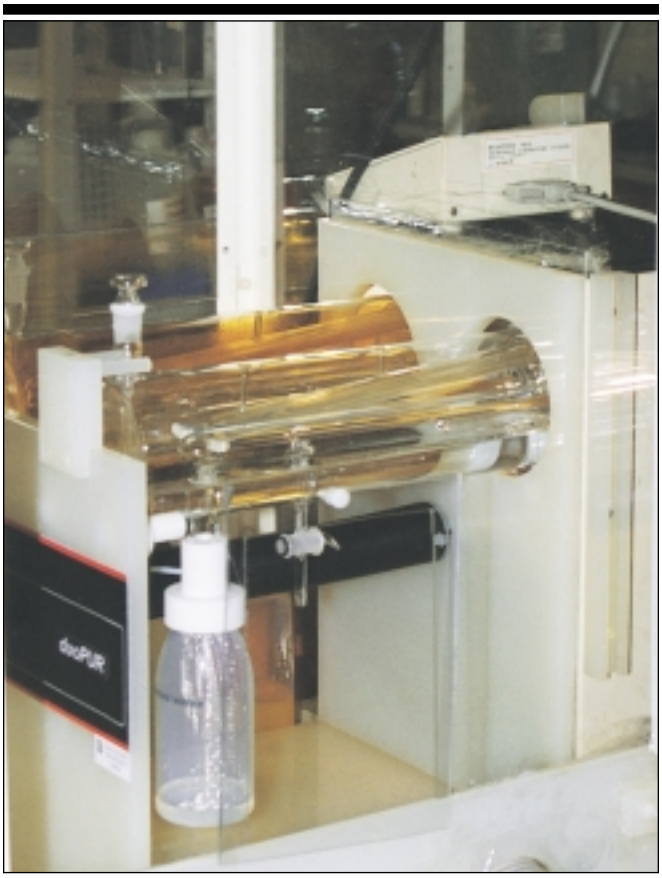

Figure 2. The subboiling distillation system setup at CMAC Laboratory.

Acid analysis. Single- and double-distilled nitric acid were analyzed for selected trace metal contamination. Table I compares the results of our analysis with Fisher Optima and Baker Ultrex II high-purity nitric acids. Our results compare favorably with the commercial acids for most contaminants. The higher contamination values for Fe, Al, Ni, and Cu suggest that corrosion from still and hood components that occurred from an accidental spill have contaminated the distillation system. We have since replaced all the corroded components and applied a fresh coat of epoxy paint to the metal still housing and expect these contamination levels to decrease in time. The contamination from Ca and Zn probably results from our analysis process and evaporation apparatus used on that particular day. The vessels used for the evaporation have been in use for 5 years on a number of projects having different levels of contamination. Even though we thoroughly cleaned the vessels before use, some apparent carryover still exists at this level of analysis. We have ordered a new set of microwave vessels so that we can repeat this experiment in virgin vessels and also test our other high-purity products. Results from our continued testing, along with any new developments, optimized distillation conditions for other

acids, and tips will be posted in the clean chemistry section of SamplePrep's Web site (6).

CONCLUSION

We have demonstrated that high-purity acids can be produced from a commercially available distillation system in a typical laboratory environment. We can produce 4.5 L of high-purity acid from 5 L of reagent-grade nitric acid for $76.18 and hydrochloric acid for $83.32 (9) (~500 mL is lost from nitrogen dioxide and chlorine gas production and when the still is drained). It would cost us $1447.40 for nitric acid and $1399.65 for hydrochloric acid (9) (two 2-L bottles plus one 500-mL bottle) to purchase the same amount of high-purity acid. This system also gives us the ability to repurify acids that have become contaminated, further adding to our cost savings. The ability to produce large volumes of high-purity acid inexpensively also allows us to use high-purity acids to clean sample bottles and microwave dissolution vessels. We have found this system to be reliable, easy to use, and a definite cost saver (the still paid for itself in 6 months), and we would recommend this option to those who are interested in doing high-precision, low-level analysis and producing high-purity acids in their laboratory.

Table I. Comparison of trace metal contamination in select high-purity nitric acids. Concentration is shown in pg/g.

Trace impurity	Duquesne single-distilled[a]	Duquesne double-distilled[a]	Fisher Optima[b]	Baker Ultrex II[c]
Be	<2	<1	<5	<20
Mg	<195	<42	<5	<100
Al	<557	<147	<20	<300
Ca	<900	<157	<50	<300
Ti	<59	<8.1	<20	<100
V	<51	<11	<1	< 20
Cr	<118	<4.6	<10	< 50
Mn	<9.7	<2.1	<1	< 20
Fe	<1000	<210	<20	<300
Co	<6	<1	<1	<20
Ni	<155	<23	<10	<100
Cu	<58	<21	<2	<50
Zn	<261	<49	<2	<100
As	<3	<0.9	<10	<100
Se	<3.9	<1.2	<10	Not listed
Sr	<12	<1.2	<1	<10
Mo	<7.1	<0.4	<1	<100
Ag	<46	<1.5	<1	<10
Cd	<8.1	<1.8	<1	<20
Sn	<22	<9.1	<10	<100
Sb	<6.1	<0.5	<10	<100
Ba	<25	<3.5	<1	<20
Tl	<2.6	<0.9	<1	<10
Pb	<10	<2.5	<1	<100

[a]Concentration expressed as the upper limit of the 99% confidence limit of the measured result (n = 4).
[b]From reference 7.
[c]From reference 8.

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