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Chemical Analysis of the Fluorine in Niobium Electropolishing

Denise C. Ford[1,2], Charlie Cooper[1], Lance D. Cooley[1], Chad Thompson[1], Donald Bouchard[3], Brian Albee[4], Sandra Bishnoi[4]

[1]Fermi National Accelerator Laboratory, Batavia, IL 60510 USA

[2]Northwestern University, Evanston, IL 60208 USA

[3]Anasazi Instruments, Inc., Indianapolis, IN 46203 USA

[4]Illinois Institute of Technology, Chicago, IL 60616 USA

email: deniseford@u.northwestern.edu

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Abstract. Surface topography and chemical purity are important factors in niobium superconducting radio-frequency (SRF) cavity performance. Electropolishing (EP) is currently being used to minimize the surface roughness and to remove the damaged surface layer created during cavity manufacturing. This process is not ideal for reasons such as safety and performance consistency, so research and development is ongoing. Furthermore, the EP process specifications have been developed empirically, and a molecular level understanding of the process is not complete. The currently employed polishing solution is composed of sulfuric and hydrofluoric acids, where the fluorine ion is active in polishing the niobium. We used vibrational and nuclear magnetic resonance (NMR) spectroscopies to analyze the standard solution, and show that fluorine is bound and released by the reaction of the acid components in the solution: $HF + H_2SO_4 <-> HFSO_3 + H_2O$. This result implies that new recipes can possibly be developed on the principle of controlled release of fluorine by a chemical reaction, which provides a route to improve the safety and effectiveness of EP. We also show that NMR or Raman spectroscopy can be used to monitor the free fluorine when polishing with the standard EP recipe.

Keywords - electropolishing, niobium, NMR, Raman, Infrared, spectroscopy, superconducting radio-frequency cavities

INTRODUCTION

The forming and processing of superconducting radio-frequency (SRF) cavities consists of many complex procedures, each of which have the capability to create defects that limit cavity performance. When the required accelerating gradient is greater than 25 MV/m electropolishing is used to remove the surface damage created by forming the cavities. The polishing is accomplished with an electric current and viscous electrolyte. The metal part to be polished is placed at the anode of the electrochemical cell, and a counter electrode is placed at the cathode. Negatively charged ions attack and dissolve the metal at the anode, while a viscous solution is used to control the diffusion of these ions and thus the polishing rate.

Electropolishing recipes are usually developed empirically. The standard recipe for niobium [1] contains a 1:9 volume ratio of 49% hydrofluoric acid, which provides the active polishing ion F^-, and 96% sulfuric acid, which provides a viscous medium to control the polishing rate. Aluminum is used for the cathode. Many studies have been performed by the SRF community to understand the effect of polishing parameters on SRF cavity performance [2-5], as well as the mechanism and quality control of the process [6-13]; however, the detailed chemistry remains elusive. Furthermore, simple inline process monitoring techniques are desired.

The chemistry of niobium electropolishing can be described as a balance between processes that oxidize the metal, processes that dissolve the oxide, and processes that occur in the electropolishing solution. It is characterized by the following reactions [14]:

electro-oxidation:

$2Nb + 5SO_4^{2-} + 5H_2O \rightarrow Nb_2O_5 + 10H^+ + 5SO_4^{2-} + 10e^-$ (1)

dissolution:

$Nb_2O_5 + 6HF \rightarrow H_2NbOF_5 + NbO_2F \cdot 0.5H_2O + 1.5H_2O$ (2)

product formation:

$NbO_2F \cdot 0.5H_2O + 4HF \rightarrow H_2NbOF_5 + 1.5H_2O$ (3)

overall:

$2Nb + 10HF + 2H_2O \rightarrow 2H_2NbOF_5 + 5H_2$ (4)

However, what actually occurs during electropolishing is much more complex. During electropolishing, Nb_2O_5 is dissolved by fluorine, and the dissolved niobium is kept in solution with a complexing agent. Niobium pentoxide is also dissolved by sulfuric acid but the reactivity is negligible compared to the action of hydrofluoric acid. Sulfuric acid, however, is efficient as a complexing agent. Numerous possible reactions involving the electropolishing solution components and niobium are listed in [15].

In this study, we use vibrational and nuclear magnetic resonance (NMR) spectroscopy to analyze the electropolishing solution. Additionally, we show that NMR or Raman spectroscopy can be used to monitor the free fluorine available for polishing with the standard recipe.

METHODS

A Renishaw, inVia, Raman microscope with a 785 nm diode laser and liquid sampling kit was used to obtain the Raman spectra at the Illinois Institute of Technology (IIT). The fluorescence backgrounds were subsequently removed by manually splining the spectra. A PerkinElmer Spectrum One Infrared spectrometer with a 633 nm laser and an attenuated total reflectance (ATR) sampling probe was used to obtain the IR spectra at Fermilab, and drifting baselines were also subsequently corrected. Some of the Raman spectra were obtained during a PerkinElmer vendor visit at Fermilab.

The NMR spectra were measured on a 60 MHz NMR instrument at Anasazi Instruments, Inc. (www.aiinmr.com) operating at 56.4 MHz for ^{19}F. Five millimeter (5 mm) sample tubes were used with teflon inserts to avoid fluorine reaction with the borosilicate glass. No volume correction was applied to the teflon inserts, but the volume differences were determined to be less than 5%. A pulse-acquire program was used to acquire the spectrum with 8 scans. The repetition rate was 4 scans per minute to allow for complete relaxation of the ^{19}F species for a total measurement time of 2 minutes. Spectra were baseline flattened and integrated with fixed integrated regions using NUTS software (www.acornnmr.com). Chemical shifts are relative to $CFCl_3$ in acetone-d6 solvent.

RESULTS

A. Raman

The spectra for freshly mixed EP solution, 96% sulfuric acid, and 49% hydrofluoric acid are shown in Figure 1. Sulfuric acid has several strong peaks in its Raman spectrum while hydrofluoric acid doesn't appear to be distinguishable. Several new peaks (810 cm^{-1} and 1082 cm^{-1}) appear, however, in the EP solution spectrum that are not present in the sulfuric acid spectrum.

Because sulfuric acid is a very strong acid, $pK_{a1} = -3$ in water, it is plausible that new peaks appear due to deprotonation upon the addition of the hydrofluoric acid solution. To test this hypothesis, we obtained the spectrum of sulfuric acid diluted with water and present the results in Figure 2. The relative intensities of the peaks in the sulfuric acid solution clearly change upon dilution, indicating differing concentrations of the ions comprising the sulfuric acid – water solutions at different concentrations. Namely, the loss of the peak at 1390 cm^{-1}, the change in the ratio between the ~915, 1050, and 1150 cm^{-1} peaks, and the growth of the peak at ~990 cm^{-1}. The peak locations and relative intensities for new the EP and sulfuric acid solutions are listed in Table 1. These spectral changes do not explain the new peaks appearing upon the mixing of sulfuric and hydrofluoric acid, however.

The Raman spectrum of hydrofluoric acid was examined further for subtle features that may be useful for analysis. The spectra at several dilutions are shown in Figure 3. Hydrofluoric acid is a very weak Raman scatterer [16]. Broad weak peaks appear around 1800 and 2200 cm^{-1} for the more concentrated hydrofluoric acid solutions, but they are clearly not suitable for tracking the fluorine concentration in dilute solutions.

Based on the Raman spectra of Gillespie and Robison [17], a potential explanation of the new peaks in the EP solution is the production of fluorosulfonic acid from the reaction of sulfuric and hydrofluoric acids. The reaction is:

$$H_2SO_4 + HF <-> H_2O + HFSO_3 \qquad (5)$$

The existence of fluorosulfonic acid in EP solution was previously determined by Eozenou, et al. [11], although they were not able to quantify it by their technique of ion chromatography.

We confirm the existence of fluorosulfonic acid in EP solution by presenting the spectra of EP solution with added fluorosulfonic acid and EP solution with added water, Figure 4. We were not able to obtain spectra of the concentrated fluorosulfonic acid due to safety and handling concerns. The spectrum of EP solution with added water is similar to the dilute sulfuric acid spectrum. Based on these spectra we can attribute the peaks at 1082 and 810 cm^{-1} to fluorosulfonic acid. Based on the published spectra in [17] we assign the peak at 1082 cm^{-1} to the FSO_3^{-1} ion, since this peak appears in their spectrum of fluorosulfonic acid with 10% added water but not in their 100% fluorosulfonic acid spectrum. Fluorosulfonic acid can be deprotonated in EP solution since it is a stronger acid than both sulfuric and hydrofluoric acids, with a pK_a of 2.64 in sulfuric acid.

The Raman spectrum of used EP solution is also shown in Figure 4. The used EP solution spectrum resembles the 96% sulfuric acid spectrum and the features representative of fluorosulfonic acid are reduced. This indicates that as free F^- is used during electropolishing, the fluorosulfonic acid that was produced upon the mixing of the solution components decomposes to produce more hydrofluoric acid, which is in turn used during the EP. Therefore, tracking the strongest fluorosulfonic acid peaks at 1082 and 810 cm^{-1} can be used as a method to track the amount of fluorine available for EP.

Additional peaks are not evident in the used EP solution spectrum to indicate the formation of any EP products. Based on the experiments of Keller [18] and von Barner et al. [19] niobium fluoride salts should have Raman and IR active vibrations in the 250-1100 cm^{-1} region. The peaks reported in [18] are listed in Table 2. Two possibilities exist for why these vibrations were not detected in this study: the concentration of the dissolved salts is too low or complexation with sulfuric acid reduces or eliminates their Raman activity.

B. Infrared Spectra

The infrared spectra of the new EP solution, 96% sulfuric acid, and 49% hydrofluoric acid are shown in Figure 5, and their peak locations and relative intensities are listed in Table 3. Several differences exist between the Raman and infrared spectra; notably, hydrofluoric acid has IR active vibrational modes. These modes, however, still do not appear in the EP solution spectrum, as the feature at ~1650 cm^{-1} is from the water

(Figure 6). As with Raman spectroscopy, peaks at 808 and 1076 cm^{-1} appear in the EP solution spectrum and can't be explained by the hydrofluoric acid dilutions (Figure 6) or the sulfuric acid dilutions (Figure 7): these peaks indicate the production of fluorosulfonic acid (Figure 8).

The IR spectrum of used EP solution is also shown in Figure 8. The predominant fluorosulfonic acid feature (808 cm^{-1}) is reduced upon use of the EP solution, indicating that this peak can be tracked by IR to monitor the EP process. Again, no new peaks appear in the used EP spectrum to indicate EP product formation.

C. NMR Spectra

The presence of fluorosulfonic acid in EP solution is also confirmed with ^{19}F NMR, and the spectra of new EP solution, new EP solution with added fluorosulfonic acid, and new EP solution with added water are shown in Figure 9. The NMR measurements allowed us to determine that new EP solution contains 1.61 mols of fluorine per kg of solution, of which 1.29 mols is bound in fluorosulfonic acid. Used EP solution, which contains ~ 2 g/l of dissolved niobium, also still contains 0.80 mols of fluorine bound in fluorosulfonic acid and only 0.01 mols of hydrofluoric acid per kg of solution. The used EP solution in this experiment does not represent completely exhausted solution. The peak near -170 ppm, which is representative of the fluorine associated with hydrofluoric acid downshifts a little in the new EP solution diluted with water. This is representative of the difference between the local chemical environment provided by each solvent as well as the differing relative concentrations of F^-, FHF^-, and

HF in each solution [20, 21]. Although F^-, FHF^-, and HF each have a unique peak location, only one peak appears in hydrofluoric acid solutions due to rapid exchange between the ions, and the peak location indicates the relative concentrations of these ions. The peak location for various ratios of sulfuric acid/water/hydrofluoric acid is shown in Figure 10.

DISCUSSION

We determined the ratio of fluorine in hydrofluoric acid to fluorosulfonic acid, R = $[HF]/[FSO_3^-]$, for various mixtures of hydrofluoric acid, sulfuric acid, fluorosulfonic acid, and water, and present the results in Table 4. We represent fluorosulfonic acid as the fluorosulfate ion, because fluorosulfonic acid is the strongest acid of the component species in the mixtures and the signature vibration of this ion was present in the Raman and IR spectra of new EP solution. Since hydrofluoric acid is a weaker acid, we represent it as HF, although its NMR signature contains contributions from HF, FHF^-, and F^-. We did not actually determine the ionization extent of either acid, and only intend to represent the balance between the fluorine related to each acid with R. We determined R to be 0.25 for new EP solution. So, initially there is a small amount of fluorine available for dissolving the niobium, and as it is used (5) runs in reverse, slowly supplying more fluorine. The equilibrium for this reaction has previously been briefly discussed in terms of niobium electropolishing by Saito et al. [2], who suggested adding fluorosulfonic acid and water to used EP solution to refresh it. The NMR results that we present in Table 4 show that water can simply be added to the EP solution to force the remaining fluorosulfonic acid to supply additional fluorine.

Via conductivity measurements, Gillespie et al. [22] determined that the equilibrium constant for (5) decreases with increasing temperature. Increasing the temperature also decreases the viscosity of the solution, therefore the free fluorine available for polishing is increased, and subsequently the etch rate, by two mechanisms. The addition of water also increases the amount of fluorine available for etching by the same two mechanisms. Our NMR data presented in Table 4 show that increasing the amount of water in the solution increases the R, and the viscosities of sulfuric acid and water are 23 cp and 0.9 cp, respectively, at 25 °C [23]. Therefore, the etch rate would increase.

Not only do these results add to the knowledge of the chemistry of EP, they also suggest that EP could be controlled by a chemical component that binds the fluorine and slowly releases it. Thus we are provided with a route to explore potential new recipes for niobium EP with fluorinated components that are safer to handle and more effective than concentrated hydrofluoric acid.

Finally, we have shown that the amount of fluorine available for polishing from the standard EP recipe can be tracked by NMR or Raman (or possibly very roughly by IR) spectroscopy. Raman spectroscopy is more suitable than IR because the differences between new and used EP solution are more striking than they are in IR and there are two fluorosulfonic acid peaks available for calibration, whereas there is only one suitable peak available in the IR spectrum. NMR provides two suitable signals in the ^{19}F spectrum for tracking.

ACKNOWLDGEMENTS

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Table 1. Raman peaks in the EP solution and sulfuric acid (SA) spectra.

New EP		1 vol. 96% SA : 0 vol. water		1 vol. 96% SA : 1 vol. water	
Location (cm^{-1})	Relative Intensity (%)	Location (cm^{-1})	Relative Intensity (%)	Location (cm^{-1})	Relative Intensity (%)
1390	4	1390	12	1210	18
1166	28	1150	38	1050	100
1082	65	1050	41	985	82
1053	68	990	20	910	40
915	100	915	100	600	47
810	8	570	49	435	48
565	65	415	40		
402	60				

Table 2. Raman and IR peaks of niobium-fluoride salts from [18].

K_2NbOF_5-H_2O (Raman)		$CsNbF_6$ (Raman)	
Location (cm^{-1})	Intensity	Location (cm^{-1})	Intensity
295	medium	280	medium
600	v. weak	562	weak
935	medium	683	strong
K_2NbOF_5-H_2O (IR, cm^{-1})		K_2NbF_7 (Raman)	
738	1626*	388	medium
932	3572*	630	v. strong
1083	3643*	782	weak

*from water of hydration

Table 3. IR peaks in new EP solution, sulfuric acid (SA), hydrofluoric acid (HFA), and water spectra.

New EP		1 vol. 96% SA : 0 vol. water		1 vol. 96% SA : 1 vol. water	
Location (cm^{-1})	Relative Absorbance (%)	Location (cm^{-1})	Relative Absorbance (%)	Location (cm^{-1})	Relative Absorbance (%)
2808	34	2849	28	3388	23
2437	29	2411	20	2893	21
2185	24	2162	12	2516	13
1660	18	1654	5	2210	9
1360	22	1348	31	1691	28
1120	67	1127	57	1291	8
1076	59	1053	31	1131	74
1036	67	941	94	1018	100
947	89	886	100	869	77
887	100	1 vol. 49% HFA : 0 vol. water		1 vol. 49 % HFA : 1 vol. water	
808	52	3484	100	3370	100
Water		~3284	~78	~3300	~95
3295	100	2779	63	~2783	~27
2114	7	2193	14	2179	1
1635	50	1755	91	1807	40
		1632	100	1630	84
		~1160	28	1175	5
		939	46	1026	8

Table 4. The fluorine distribution in mixtures of 96 % sulfuric acid (SA), 49 % hydrofluoric acid (HFA), fluorosulfonic acid (FSA), and water determined from ^{19}F NMR measurements.

Initial Volume Ratios of Components in the Mixtures				$[HF]/[FSO_3^-]$
SA	HFA	FSA	Water	
0.900	0.100	0.000	0.000	0.25
0.891	0.099	0.010	0.000	0.24
0.855	0.095	0.050	0.000	0.21
0.720	0.080	0.200	0.000	0.11
0.720	0.080	0.000	0.200	6.26

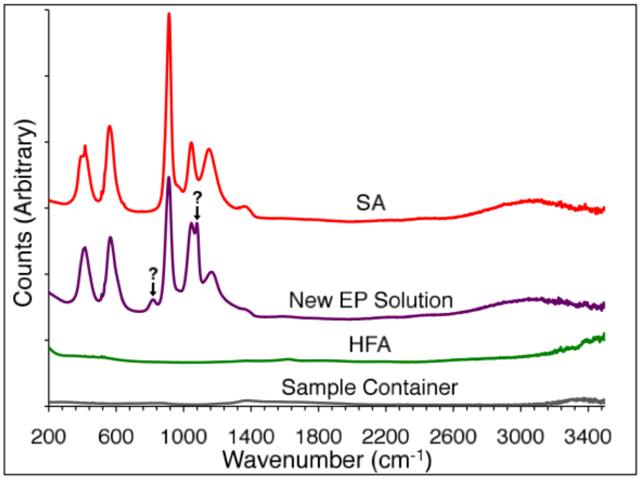


Figure 1. Raman spectra of new (unused) EP solution, its components (49 % hydrofluoric acid in water (HFA) and 96 % sulfuric acid (SA)), and the sample container. The spectra are plotted with an offset for clarity. The question marks/arrows indicate peaks in the new EP solution spectrum that cannot be explained by the separate component spectra.

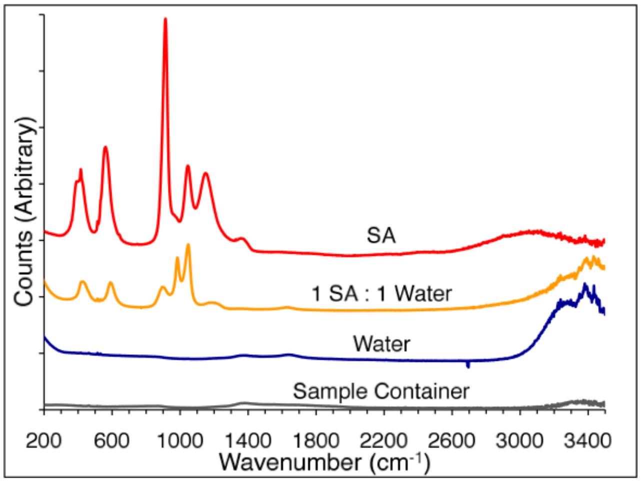
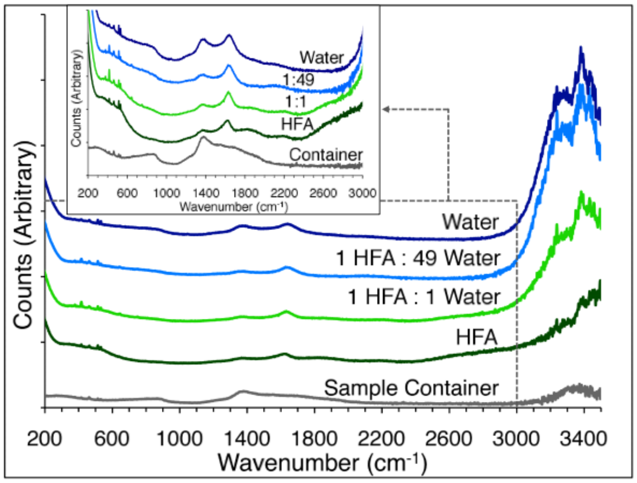


Figure 2. Raman spectra of 1 volume 96% sulfuric acid (SA) diluted with 1 volume water. The spectra of 96 % sulfuric acid (component of EP solution), water, and the sample container are shown for reference. The spectra are plotted with an offset for clarity.



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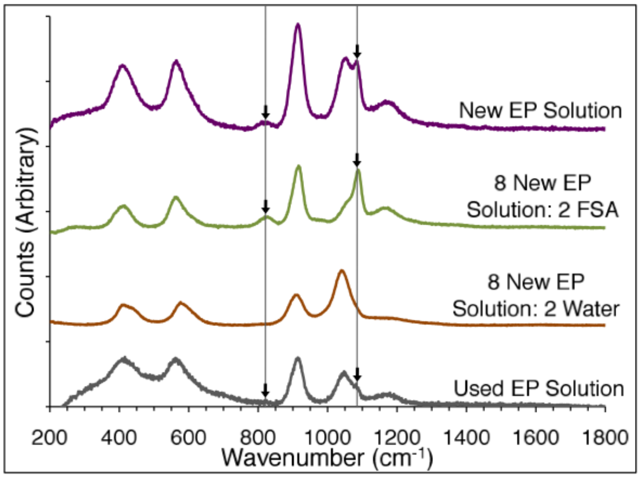


Figure 4. Raman spectra of new (unused) EP solution, 80 vol. % EP solution + 20 vol. % fluorosulfonic acid (FSA), 80 vol. % EP solution + 20 vol. % water, and used EP solution. The spectra are plotted with an offset for clarity. The arrows indicate peaks in the new and used EP solution spectra that are explained by the addition of fluorosulfonic acid.

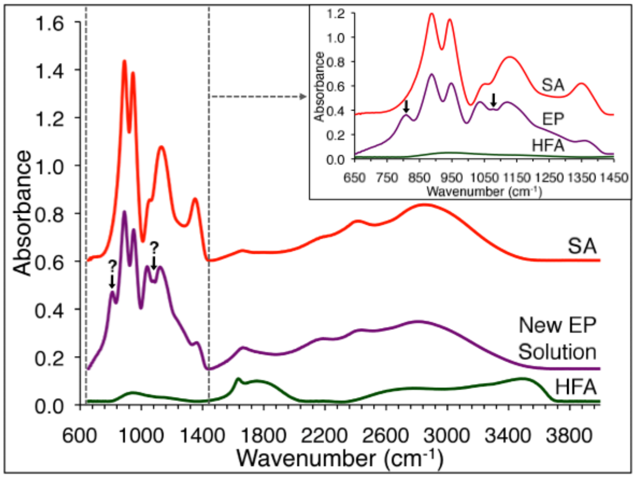


Figure 5. Infrared spectra of new (unused) EP solution and its components (49 % hydrofluoric acid (HFA) in water and 96 % sulfuric acid (SA)). The spectra are plotted with an offset for clarity. The inset shows an expansion of the region 650-1450 cm^{-1} to emphasize the differences between new EP solution and its individual components. The question marks/arrows indicate peaks in the new EP solution spectrum that cannot be explained by the separate component spectra.

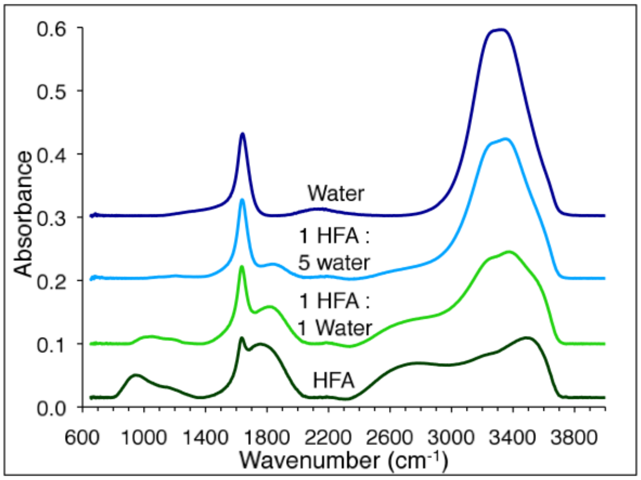


Figure 6. Infrared spectra of 49 % hydrofluoric acid (HFA) diluted with water; the ratios are by volume. The spectra of 49 % hydrofluoric acid (component of EP solution), and water are shown for reference. The spectra are plotted with an offset for clarity.

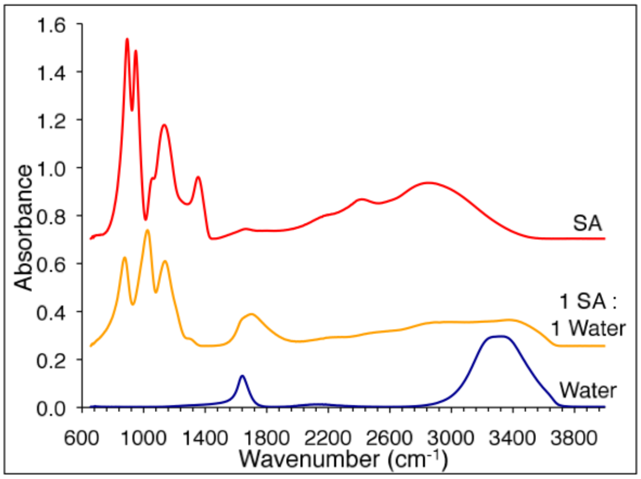
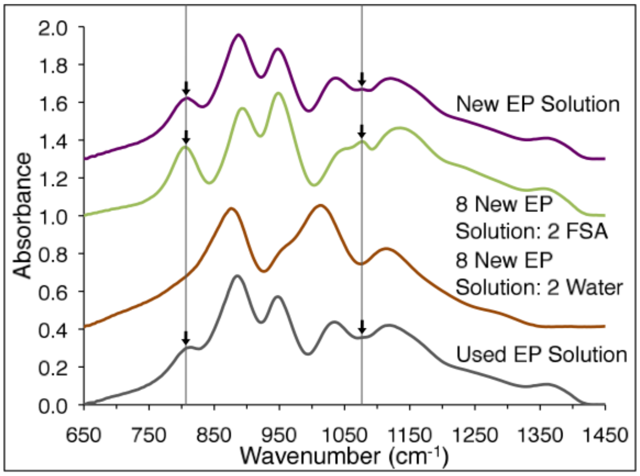


Figure 7. Infrared spectra of 1 volume 96% sulfuric acid (SA) diluted with 1 volume water. The spectra of 96 % sulfuric acid (component of EP solution) and water are shown for reference. The spectra are plotted with an offset for clarity.



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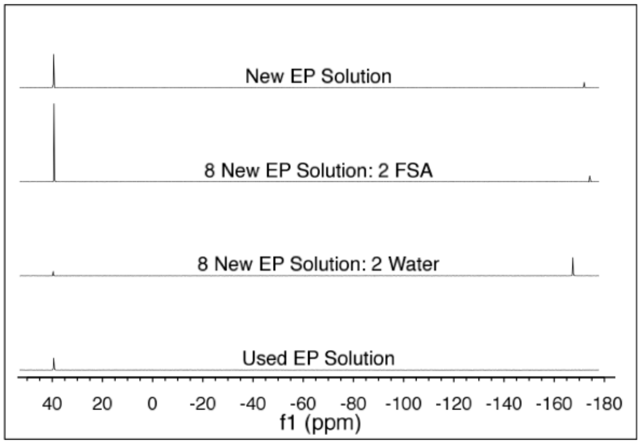

Figure 9. ^{19}F NMR spectra of new (unused) EP solution, 80 vol. % EP solution + 20 vol. % fluorosulfonic acid (FSA), 80 vol. % EP solution + 20 vol. % water, and used EP solution. The peak near 40 ppm indicates fluorosulfonic acid and the peak near -170 ppm indicates hydrofluoric acid.

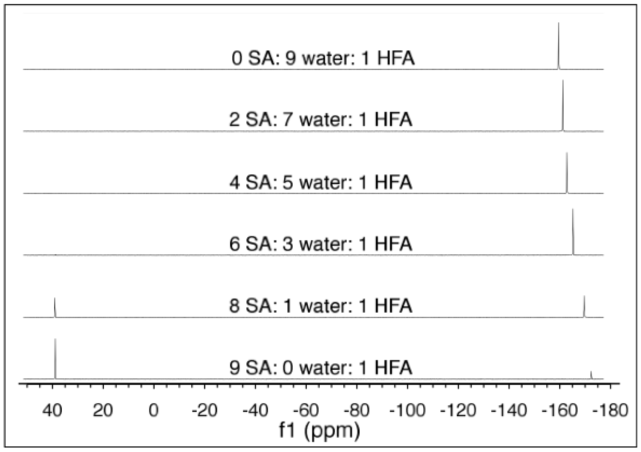

Figure 10. ^{19}F NMR spectra of 48 % hydrofluoric acid (HFA) diluted with various amounts of water and 95 % sulfuric acid (SA); the ratios are by volume. The peak near 40 ppm indicates fluorosulfonic acid and the peak near -170 ppm indicates hydrofluoric acid.

Table Captions

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