

UPDATE ON QUALITY CONTROL OF ELECTRO POLISHING ACID

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Abstract

Electro-polishing has become one of the leading surface preparation processes to reach high gradients in superconducting cavities. For industrialization and for reproducible results in the electro-polishing process a study on acid quality control and quality management was launched under the scope of the European investigations under the CARE. First results of this acid management studies were presented at the TTC meeting 2006 and the JRI-SRF summary reports 2008. A second study with experimental results on the quality control methods proposed was launched where the different methods and instrumentations for acid quality control are studied in detail. We present the results of this following up investigations made on acid quality control for the electro-polishing mixture applied at DESY.

INTRODUCTION

Since start up of electro polishing (EP) at DESY and during the start up of industrial electro polishing [1] it is found that variations of the acid components result in variation of the polishing process. The consumption (Aging) or the evaporation of the hydro fluidic component during the mixing process is origin of variation of the mixture [2].

Acid mixture variations of about 5 % of the basic mixture [3] prescription result in process variations of material removal per time unit ($\mu\text{m}/\text{min}$) and hence in process duration. For industrial application this variation and the need of an associated subsequent cavity treatment is not acceptable. To set up an acid quality management for the EP acid, an industrial study was started. Basing on this analysis of analytical methods [4] a second part of the study is launched, where the applicability of the methods is studied. In order to evaluate the potential of each analysis method a calibration acid mixture as well as defined variations of this mixture and resetting sample from industrial production are in use [Table 1].

In a first step the reproducibility of the methods is studied on the reference mixture (Sample 1 to 3). To investigate the sensitivity of the methods, they are applied on composition with well defined variations in the amount of Hydro Fluoride (HF) and variations in the mixing process where the temperature of the acid during mixing is kept stable in different regimes (sample 1 to 10)

Table 1: specification of the acid mixtures in use for evaluation of analysis methods

Sample Nr.	Notes	min. temp.	max. temp.	remarks
1	Cold	14	21	
2	Cold	12	19	
3	Cold	12	20	
4	-10% HF	11	19	
5	-20% HF	11	18	
6	+10% HF	10	18	
7	+20% HF	9	18	
8	Warm	20	45	fume evap.
9	Warm	21	47	fume evap.
10	Warm	20	48	fume evap.
11	Used			(main EP)
12	Used			(main EP)
13	Used			(main EP)
14	Used + silicon oil			(main EP)
15	Used + silicon oil			(main EP)
16	Used + silicon oil			(main EP)
17	Warm	19	46	fume evap.
18	Warm	18	47	fume evap.
19	Used (2main ep)			
20	Cold + polish	9	19	
21	Cold + sulfur	8	18	

ICP-OES AND TOC MEASUREMENTS

Inductively coupled plasma optical emission spectrometry (ICP-OES), is a commonly in use analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that makes use of the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element.

Total organic carbon (TOC) is the amount of carbon bound in an organic compound which can be oxidized and measured.

Measurements on Different Acid Sample Mixtures

For all sample mixtures the amount of metallic impurities and the TOC value are determined. It is found, that the metallic contaminations of the mixtures which are made from pure basic components (pro analysis) do not vary (Table 2). For used acids which have been in contact with softeners imbedded in PVC tubes or contaminated with silicon oil, increased TOC value are measured.

Table 2: Results of the ICP-OES and TOC Measurement

	REMARKS	Nb	Na	K	Mg	Ca	Fe	Cr	Ni	Al	TOC
Sample 1	cold	<1	<1	<1	<1	<1	<1	<1	<1	<1	50
Sample 2	cold	<1	<1	<1	<1	<1	<1	<1	<1	<1	52
Sample 3	cold	<1	<1	<1	<1	<1	<1	<1	<1	<1	69
Sample 4	cold -10%HF	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Sample 5	cold -20%HF	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Sample 6	cold +10%HF	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Sample 7	cold +20%HF	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Sample 8	warm	<1	<1	<1	<1	<1	<1	<1	<1	<1	61
Sample 9	warm	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Sample10	warm	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Sample11	used										110
Sample12	used										139
Sample13	used										130
Sample14	used +Siliconoil										110
Sample15	used +Siliconoil										91
Sample16	used +Siliconoil										122
Sample19	2" 9 cell cavity	4950	<1	<1	<1	2	8	<1	<1	<1	<50
Sample20	cold + polish	4700	<1	<1	<1	<1	12	<1	<1	<1	<50
Sample21	cold +Sulfur										<50

Evaluation of the Methods

ICP-OES is a suitable analysis method to analyze impurities in very small quantities (ppm). Several, mostly metallic elements can be analyzed in the same run. One major drawback is that the chemical compounds can't be analyzed directly, they will be cracked into elements by the plasma (4000-5000 K). A high dilution is necessary and can only be done in well equipped laboratories.

TOC is suitable to investigate organic impurities like softener from material in use for pipes of the installations or organic oils. A high dilution of the acid is necessary and the measurements can only verify that there are oxidizable substances. This method does not allow determining the kind of impurities.

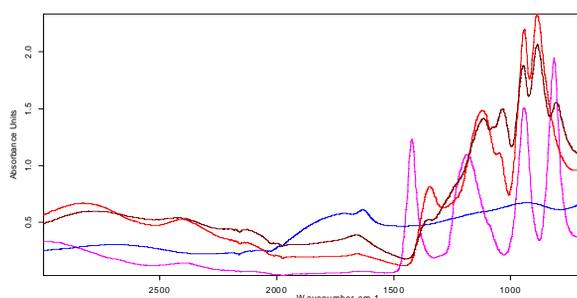
Both analysis methods are limited in applicability on the quality control of the EP acid, but allow as statically analysis of the basic components in use and the purity of the process.

FTIR-ATR (FOURIER TRANSFORM INFRARED SPECTROSCOPY ATTENUATED TOTAL REFLECTANCE)

Attenuated total reflectance (ATR) is a sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation. ATR uses a property of total internal reflection called the evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample, typically by a few micrometers. This beam is collected by a detector as it exits the crystal. This evanescent effect works best if the crystal is made of an optical material with a higher refractive index than the sample being studied.

Allocation of the Chemicals

In order to assign the peaks to the chemical compound, a calibration of the wave length is made by pure and well known chemical compounds (Fig.1). A problem introduced by adding components is shifting the peaks by changing the acid composition.



Sample 1 H₂SO₄ 96% HF 48% FSO₃H 100%

Figure 1: Measurement to allocate the chemicals.

Reproducibility of the FTIR-ATR Method

For the FTIR-TAR probe in use the peak height reproducibility in the absorption unit (absu) range from 1,42 to 1,50 (absu) of $\pm 0,012$ (<1%) is found for the three samples of identical composition (Fig.2). For sample 1 the HF peak is determined at 1,5 absu. An increase of HF by 10 percent shifts this peak to 1,483 absu, the increase of 10 % of HF show that peak 1,530 absu.

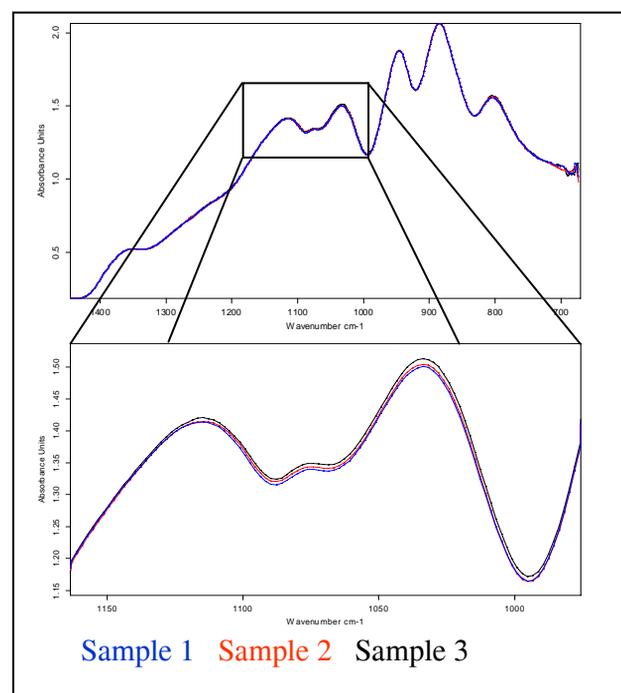


Figure 2: Reproducibility measurement for three different samples. Bottom 1/ 4.25 magnification.

Measurements of the Sample Mixtures

Only in the case of a deviation of the hydrofluoric acid concentration of more than 10% reproducible variation in signal height is found (Fig.3). A distinction between cold and warm mixed acid was not possible within the sensitivity range of the probe.

Evaluation of the Method

The advantage of this analysis method is the easy handling and the fast response of data in undiluted

electrolytes on the place of application. A measurement is performed in fewer 30 seconds. The sensitivity for acid component variation is limited an only strong variation can be found by this method.

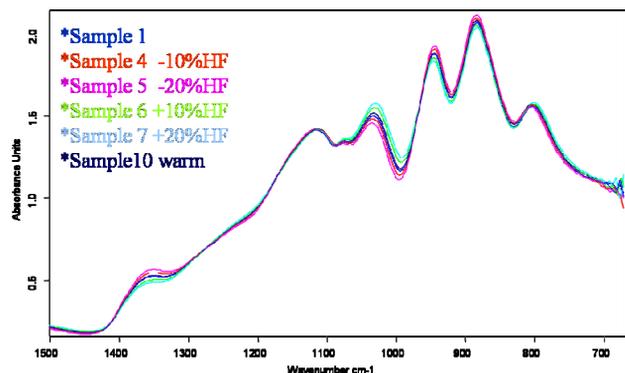


Figure 3: Sensitivity of the FTIR to variation of HF concentration.

ITP (ISOTACHOPHORESIS)

Isotachopheresis is a technique in analytical chemistry used to separate charged particles. It is an advancement of the electrophoresis. It is a separation technique using a discontinuous electrical field to create sharp boundaries between the sample constituents. After applying an electric potential a low electrical field is created in the leading electrolyte and a high electrical field in the terminating electrolyte.

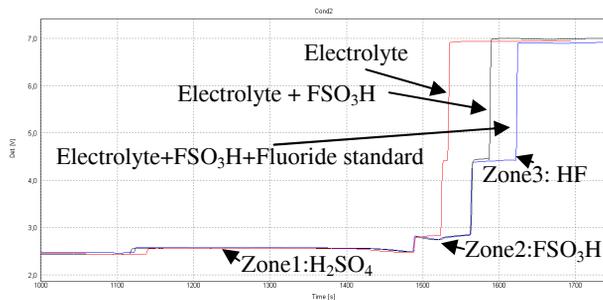


Figure 4: results of the ITP (isotachopheresis); x scale Run time signal (sec); y scale voltage applied (V).

Measurements on the Samples

For calibration the individual components are added to the electrolyte and the different run times zones can be determined. (Fig.5). The samples analysis shows that this methods results in high separation of the components (Tab.3) reproducibility in a range of less then 3% In the measurements made variations of the HF content is measured (Samples 1-3; 8-10), but these numbers do not allow to determine the origin of the shift

Evaluation of the Method

The ITP analysis allows differentiating components precisely. With this method show variations for composition changes (sample 4-7) and a temperature dependency for the mixing process (1-3; 8-10). These data do not allow distinguishing, whether the variation

results from the mixing process or an error in composition.

Table 3: Results of ITP Measurements

Sample nr.	notes	H2SO4 ml	HF ml	Time Zone 1 in sec.	Time Zone 2 in sec.	Time Zone 3 in sec.	Content H2SO4 in g/l	± Deviation H2SO4 (2,64%) in g/l	Content HF in g/l	± Deviation HF (2,64%) in g/l
1	cold	450	50	353,12	42,16	8,48	1395,45	36,84	13,32	0,35
2	cold	450	50	345,12	41,68	7,88	1356,02	35,80	12,20	0,32
3	cold	450	50	344,12	44,04	8,24	1351,09	35,67	12,87	0,34
4	cold-10%HF	450	45	363,24	39,08	6,48	1445,34	38,16	9,58	0,25
5	cold-20%HF	450	40	361,24	34,36	5,68	1435,48	37,90	8,08	0,21
6	cold+10%HF	450	55	335,68	44,96	8,60	1309,48	34,57	13,54	0,36
7	cold+20%HF	450	60	323,20	46,56	12,72	1247,96	32,95	21,26	0,56
8	warm	450	50	343,72	37,32	7,00	1349,12	35,62	10,55	0,28
9	warm	450	50	341,68	36,76	6,88	1339,06	35,35	10,32	0,27
10	warm	450	50	341,01	39,08	6,92	1335,76	35,26	10,40	0,27
17	warm+12%HF	450	56	338,04	47,60	11,04	1321,11	34,88	18,11	0,48
18	warm+6%HF	450	53	344,96	37,44	8,80	1355,23	35,78	13,92	0,37

SUMMARY

In a first study for setting up an acid management and control for the EP mixtures in use at DESY, several analysis methods were examined in order to find a suitable method applicable in an industrial production as well. In this second part of the acid management study the most promising methods were examined in detail. A special attention is set on the applicability of the methods in an industrial application where the quality control should be made with fast response time in order not to have too high temporary storage further.

The methods investigated here on different niobium electro polishing electrolytes showed that all methods are insensitive to small changes in the composition of the electrolyte. During the polishing processes at DESY it was found that the process and plant parameters are correlated to the temperatures at which the acid is mixed. No significant difference between cold produced electrolyte (below 20°C) and warm produced electrolyte (above 45°C) is found in this study with the methods analysed here. The most promising method for industrial application, the FTIR ATR method can be applied locally in the field with easy handling and does not need dilution of the acid. The sensitivity is limited and no difference for fabrication errors with 10 % deviation of concentrations is found here. The need high dilution determines the accuracy of some of the methods. None examined analysis methods is without reservation suitable for quality control.

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