Fluoride Analysis by Ion Chromatography

By Terry Munson (Terrym@residues.com)

In many cases ion chromatography is an effective tool when measuring the amount of ionic residues from paste, liquid flux and hand solder on a PCBA that has been exposed to 1 to 3 thermal excursions. Each residue detected must be looked at with an educated eye for things that can co-elute with each of the columns and separation techniques utilized in the analysis. Issues with fluoride analysis are typically misidentified. Fluoride has a low molecular weight and valence charge and is not retained by the columns in the normal elution times for ions like chloride, nitrate or sulfate. Also, fluoride is easily volatized under normal reflow temperatures and is rarely detected on PCBA assemblies. Using the standard Anion Column technology, AS4A-SC, AS14, AS18, and AS22, a typical fluoride peak will come out of the water dip because it is such a weak acid. We have found that organic acids that are not completely dissociated or the abietic acid will co-elute with fluoride. We use HPLC (High Pressure Liquid Chromatography) from Dionex, utilizing UV-Vis detection, to complement the ion chromatography systems. We have also found that with the 80^{o}C, one hour extraction more organic material is brought into the sample. With the C3 extraction we are not seeing this organic breakdown of the sample.

With ion chromatography the separation is created by the column's resin chemical composition holding like species together. As unknown samples are introduced into the column, a chemical separation is created in the eluent stream. The amount of ionic and organic residue (all conductive because they show up on the conductivity detector) separates and washes down the column in like species based on molecular weight and valence charge strength. Residues that are not well retained by the column charge will be displayed as a conductive peak just out of the water dip. Water is at a different conductivity than the eluent so we know exactly when the water passes through the column and is not retained on the column. The water dip will be detected, and then residues that are not easily retained will wash off directly out of the water dip. This is the retention time that fluoride washes off the column. This can be seen in the Fig 1 chromatogram showing Sample A with residue coming out of the water dip with no delay. This fluoride peak should not be taken on face value. Historically, we would run a weaker eluent to push the retention times further away from the water dip. Using a weaker eluent, we can push the retention time from 1.83 minutes to 3.87 minutes displaying a clearer separation.

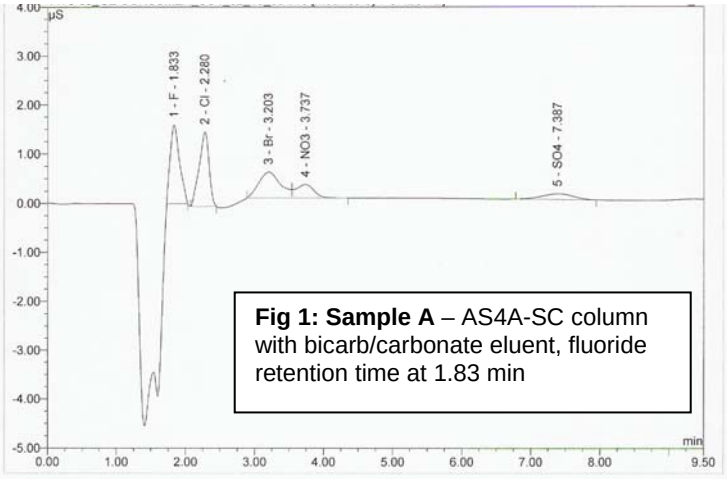

Fig 1: Sample A – AS4A-SC column with bicarb/carbonate eluent, fluoride retention time at 1.83 min

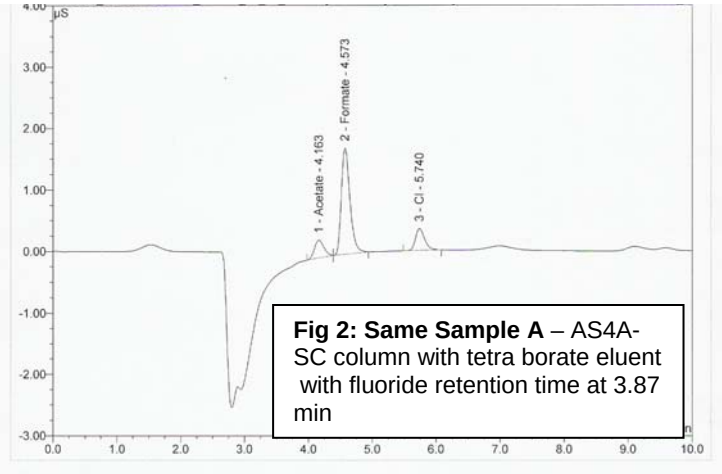

Fig 2: Same Sample A – AS4A-SC column with tetra borate eluent with fluoride retention time at 3.87 min

We see in Fig 2 that Sample A separated into a small acetate and large formate peak when the weaker eluent was utilized. So what would have been reported as a fluoride peak becomes acetate and formate peaks with additional analysis. Both acetate and formate can be found in some soldermask materials and can be extracted during an aggressive bag extraction.

Using improved column technology and modification of the eluent we have found that the ionic residues can be separated from the organic residues in one 17 minute run, as seen below in Fig 3. The AS22 allows for nearly 1 minute of separation from the water dip to the fluoride peak. A lack of understanding and verification of the organic residues that are not well retained by the column and where they will present at the detector retention time can result in fluoride being easily misidentified.

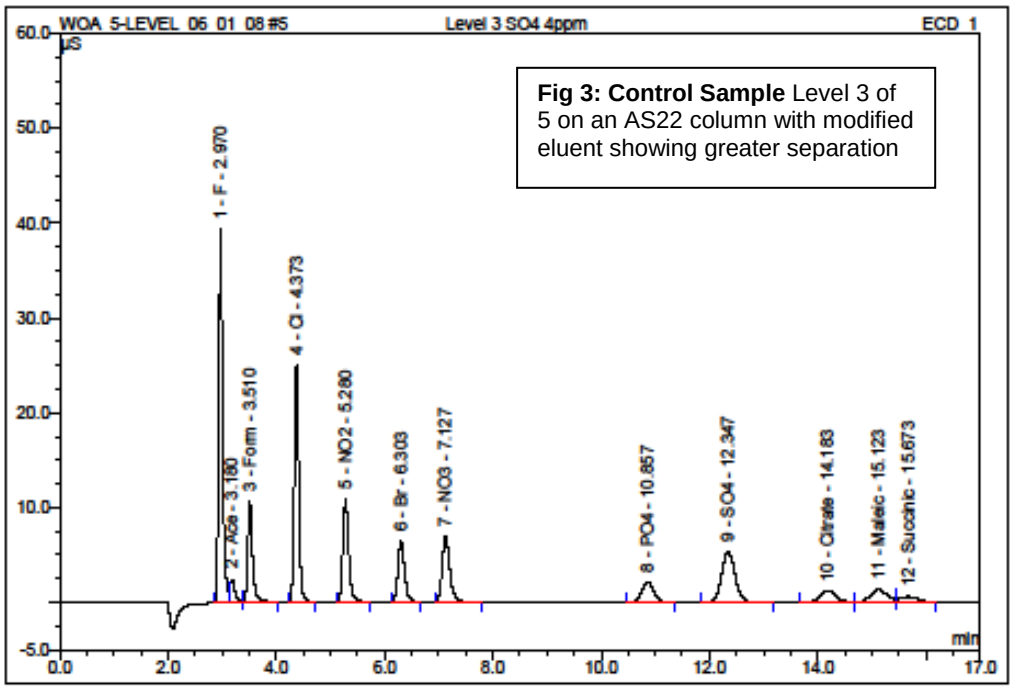

Fig 3: Control Sample Level 3 of 5 on an AS22 column with modified eluent showing greater separation