Electroplating mystery compound

April 26, 2024

The goal of this project is to use NMR to support MS for environmental discovery. We have come across 2 mystery compounds we cannot assign, but need to find out what they are. The standard MS analyses don't seem to be picking them up.

What we know.

We have mystery compound (or 2 compounds). It is specific to the electroplating industry and we find it in their effluents.

It is in some but not all electroplating effluents, so we assume it is specific to a particular electroplating process.

We are not allowed to know details as to the industries, this is just an exploratory project to explore the potential of NMR. All we know are

- Description provided for site 1: "Electroplating"
- Description provided for Site 2: "Electroplating – gold, silver, copper, nickel"

See arrows on the spectra on the next page.

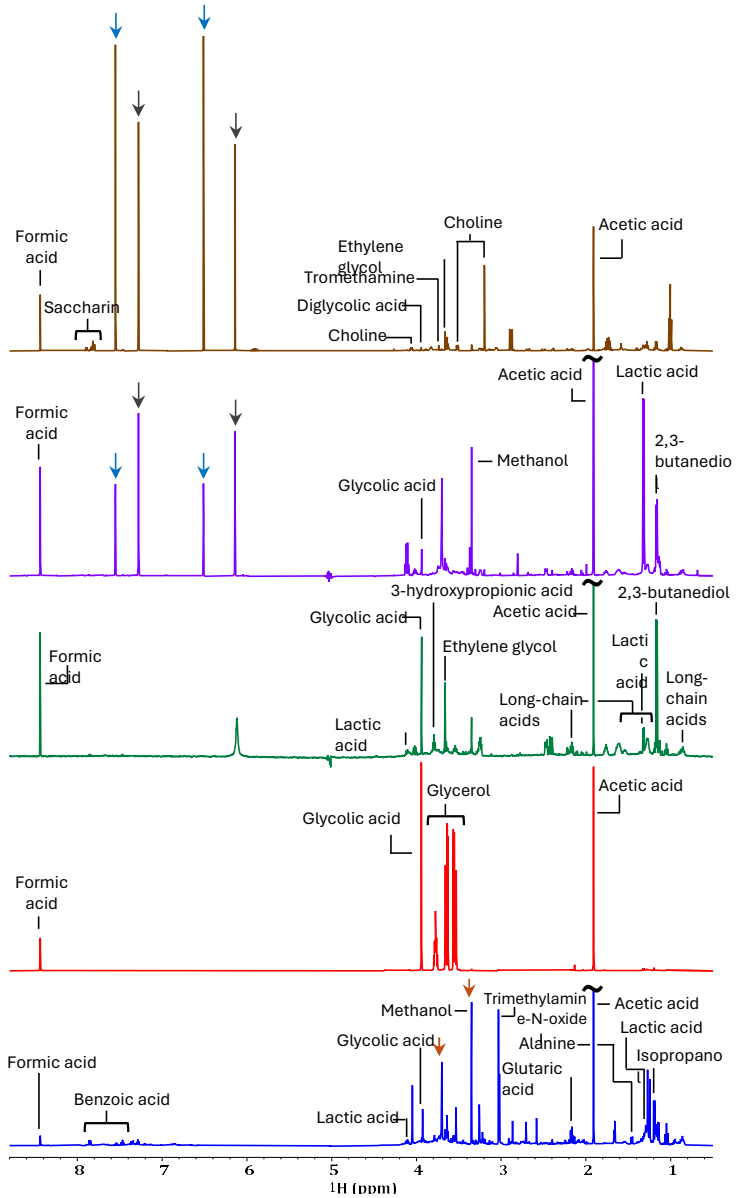
Choline and Saccharin are apparently brighteners added in Nickel plating, but we do not know if they are specific to Nickel plating.

Electroplating sites – with labels.

500 MHz (prodigy cryo), unconcentrated, straight from the discharge pipe into the NMR tube. So these things are pretty concentrated.

The peaks with arrows are the ones of interest.

Other electroplating effluents. Either these industries have cleaned up the compounds before discharge, or they are a different process that does not use them.



Notes:

Largest peaks in spectra so pretty concentrated

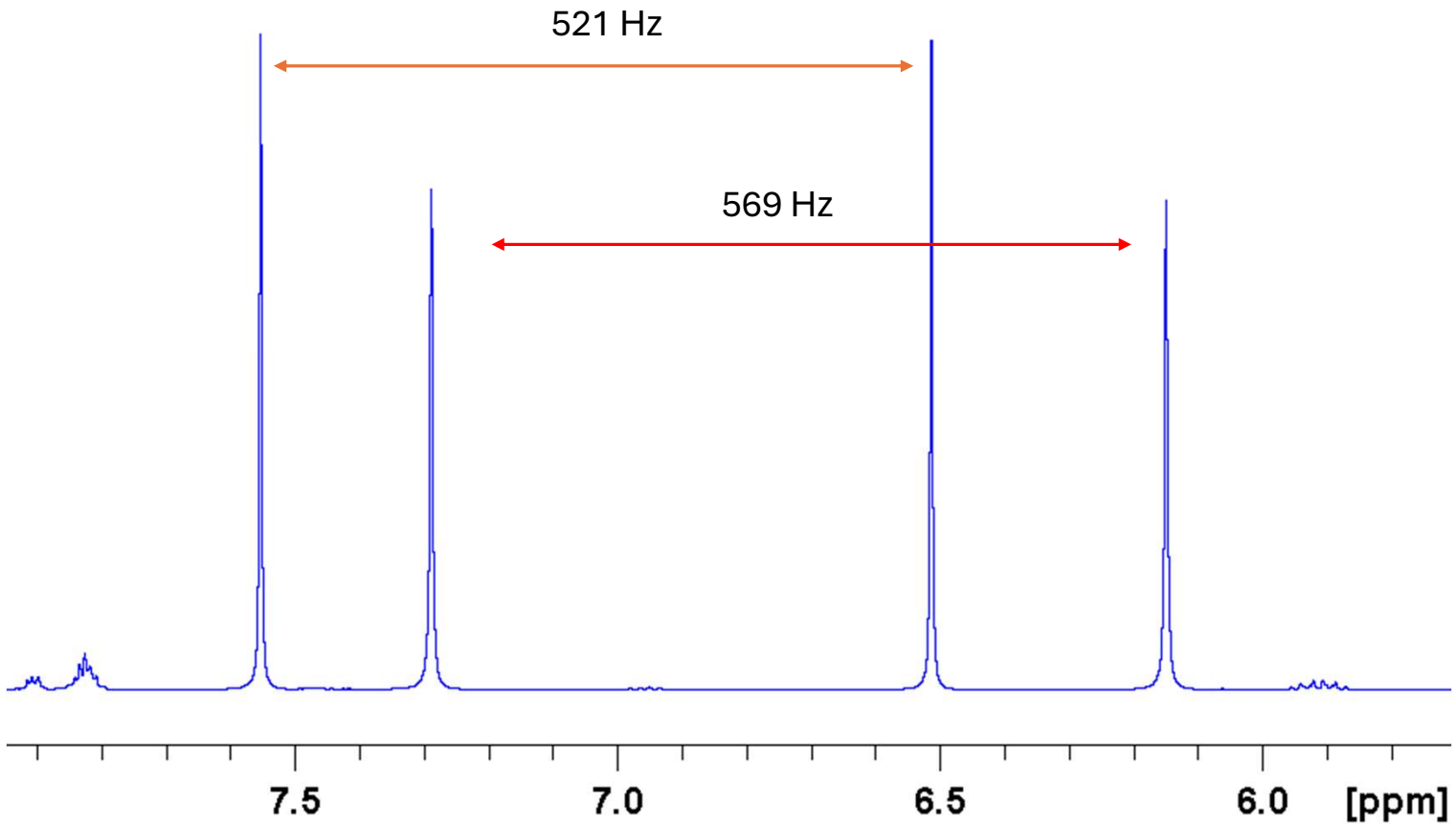
- Samples in ~90:10 H_2O:D_2O
- No correlations shown in 1H-13C HSQC, HMBC, or 1H-1H COSY or 1H-1H TOCSY.
- Not connected to carbon
- Do not disappear in pure D2O, indicating they are not exchangeable.
- 1H-1H JRES does not suggest J coupling

- However, the peaks do seem to be split pairs.

- They are separated by 521 Hz and 569 Hz (see next slide)

- This “splitting” 521 Hz and 569 Hz seems to be field independent, it remains the same at 80MHz.
- Do not seem to shift significantly with temperature

Is this some sort of quadrupole splitting from a metal complex of some sort ? There are some funky metals used in plating. Metal cyanides are common. Anyone got any ideas we are stumped ? The metals in the samples on on the next page. But nothing is jumping out.


521 Hz
569 Hz
7.5
7.0
6.5
6.0
[ppm]

Metals analysis – Nitric and hydrochloric acid digestion of effluents followed by analysis by ICP-OES

Site 1			Date Collected:	10/19/2021 7:00:00 AM	
Analyte	**Result**	**Rmk**	**RDL**	**Units**	**Analyzed**
Metals					
Aluminum	<0.030		0.030	mg/L	11/10/2021
Antimony	<0.050		0.050	mg/L	11/10/2021
Arsenic	<0.050		0.050	mg/L	11/10/2021
Barium	0.0475		0.0050	mg/L	11/10/2021
Beryllium	<0.0040		0.0040	mg/L	11/10/2021
Boron	6.01		0.20	mg/L	11/10/2021
Cadmium	<0.0030		0.0030	mg/L	11/10/2021
Calcium	61.0		0.020	mg/L	11/10/2021
Chromium	0.247		0.010	mg/L	11/10/2021
Cobalt	<0.0050		0.0050	mg/L	11/10/2021
Copper	0.0913		0.0050	mg/L	11/10/2021
Iron	<0.050		0.050	mg/L	11/10/2021
Lead	<0.020		0.020	mg/L	11/10/2021
Magnesium	2.01		0.020	mg/L	11/10/2021
Manganese	<0.0030		0.0030	mg/L	11/10/2021
Molybdenum	<0.010		0.010	mg/L	11/10/2021
Nickel	0.113		0.010	mg/L	11/10/2021
Potassium	5.35		0.20	mg/L	11/10/2021
Selenium	<0.050		0.050	mg/L	11/10/2021
Silver	<0.0060		0.0060	mg/L	11/10/2021
Sodium	996		0.10	mg/L	11/10/2021
Strontium	0.202		0.0050	mg/L	11/10/2021
Titanium	<0.0050		0.0050	mg/L	11/10/2021
Vanadium	0.00500		0.0050	mg/L	11/10/2021
Zinc	0.00550		0.0050	mg/L	11/10/2021
Hardness	160		0.20	mg/L	11/10/2021

Site 2			Date Collected:	10/19/2021 7:00:00 AM	
Analyte	**Result**	**Rmk**	**RDL**	**Units**	**Analyzed**
Metals					
Aluminum	0.741		0.030	mg/L	11/10/2021
Antimony	<0.050		0.050	mg/L	11/10/2021
Arsenic	<0.050		0.050	mg/L	11/10/2021
Barium	0.00500		0.0050	mg/L	11/10/2021
Beryllium	<0.0040		0.0040	mg/L	11/10/2021
Boron	0.251		0.20	mg/L	11/10/2021
Cadmium	<0.0030		0.0030	mg/L	11/10/2021
Calcium	20.5		0.020	mg/L	11/10/2021
Chromium	<0.010		0.010	mg/L	11/10/2021
Cobalt	<0.0050		0.0050	mg/L	11/10/2021
Copper	0.131		0.0050	mg/L	11/10/2021
Iron	<0.050		0.050	mg/L	11/10/2021
Lead	<0.020		0.020	mg/L	11/10/2021
Magnesium	2.23		0.020	mg/L	11/10/2021
Manganese	<0.0030		0.0030	mg/L	11/10/2021
Molybdenum	<0.010		0.010	mg/L	11/10/2021
Nickel	0.0839		0.010	mg/L	11/10/2021
Potassium	21.2		0.20	mg/L	11/10/2021
Selenium	<0.050		0.050	mg/L	11/10/2021
Silver	<0.0060		0.0060	mg/L	11/10/2021
Sodium	380		0.10	mg/L	11/10/2021
Strontium	0.114		0.0050	mg/L	11/10/2021
Titanium	<0.0050		0.0050	mg/L	11/10/2021
Vanadium	0.00650		0.0050	mg/L	11/10/2021
Zinc	0.0219		0.0050	mg/L	11/10/2021
Hardness	60.3		0.20	mg/L	11/10/2021

Other Analysis in case it helps

Analyte	Sample 1	Sample 2	Units
4-Nitrophenol	<	0.7	µg/L
Alkalinity	210	72.6	mg/L as CaCO3
Aluminum	0.741	<	mg/L
Barium	0.005	0.0475	mg/L
Boron	0.251	6.01	mg/L
Bromodichloromethane	5.2	<	µg/L
Calcium	20.5	61	mg/L
Carbon; dissolved inorganic	32.5	9.85	mg/L
Carbon; dissolved organic	8.17	9.57	mg/L
Chlorodibromomethane	2.5	<	mg/L
Chloroform	62	27	µg/L
Chromium	<	0.247	mg/L
Conductivity	1900	4570	µS/cm
Copper	0.131	0.0913	mg/L
Fluoride	0.33	0.85	mg/L
Hardness	60.3	160	mg/L

Analyte	Sample 1	Sample 2	Units
L-PFDS	<	0.9	ng/L
L-PFHxS	<	2.5	ng/L
L-PFOS	17	2400	ng/L
Magnesium	2.23	2.01	mg/L
Nickel	0.0839	0.113	mg/L
Nitrate	63.5	131	mg/L
Nitrogen; ammonia+ammonium	0.96	22.2	mg/L
Nitrogen; nitrate+nitrite	63.5	134	mg/L
Nitrogen; nitrite	0.07	3.71	mg/L
PFBA	5.9	5	ng/L
PFDA	11	<	ng/L
PFDoA	1.7	<	ng/L
PFHpA	4.2	26	ng/L
PFHxA	16	19	ng/L
PFNA	3.6	0.5	ng/L
PFOA	11	2.4	ng/L

Analyte	Sample 1	Sample 2	Units
PFPeA	5	7.3	ng/L
PFUnA	1.9	<	ng/L
pH	9.96	8.51	-
Phenol (E3179)	1.48	3.65	µg/L
Phenol (E3265)	<	1	µg/L
Phosphorus; phosphate	0.506	0.158	µg/L
Phosphorus; total	4920	16400	µg/L
Potassium	21.2	5.35	mg/L
Silicon; reactive silicate	7.6	0.96	mg/L
Sodium	380	996	mg/L
Strontium	0.114	0.202	mg/L
Sulphate	13.8	27.3	mg/L
Trihalomethanes-total	690	270	µg/L
Vanadium	0.0065	0.005	mg/L
Zinc	0.0219	0.0055	mg/L