Direct Analysis of Cross Linking Agents in Chloroform and Other Volatile Solvents Using ICP-OES

Greg Gilleland[1] and Paul Krampitz[1]

1. Agilent Technologies, Santa Clara, CA

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Introduction

Cross-linked polymers have been used in a variety of industries for more than 170 years. Beginning with Charles Goodyear's accidental vulcanization of rubber using sulfur and heat to polymers engineered for physical and chemical properties to be used in everything from construction to arterial stents, crosslinkers have been used to develop new materials and open new frontiers.

This work was undertaken as a result of a customer request to investigate whether the Agilent 5110 ICP-OES was capable of analyzing a crosslinker (N,N'-Methylenebisacrylamide) in chloroform. It was determined that the material exhibited poor solubility in chloroform but was soluble in methanol. We continued the work with methanol but also pursued the analysis of chloroform to satisfy our own curiosity.

Experimental

All measurements were made using the Agilent SVDV 5110 ICP-OES. Sample introduction consisted of a SeaSpray Nebulizer (Agilent; Cat # G8010-60255) and a semi-volatile torch (Agilent; G8010-60233) and an IsoMist Temperature-Controlled Spray Chamber (Agilent; Cat # G8486A #100). Instrument operating conditions are shown in Figure 1.

Parameter	Methanol	Chloroform
Bkgrd Correction	Fitted/FACT	Fitted/FACT
Nebulizer	SeaSpray	SeaSpray
Spray Chamber	IsoMist	IsoMist
Plasma View	SVDV	Axial/Radial
Replicates	3	3
Pump Speed	10	12
Sample Tubing	Blk/Blk Marprene	Blk/Blk Viton
Waste Tubing	Blue/Blue PVC	Blue/Blue Viton
Power	1.40kW	1.50kW
Read Time	20 sec	10 axial/5 radial
Viewing Height	12 mm	12 mm

Table 1 – Instrument and Sample Intro Conditions

Experimental

Multiple aliquots of N,N'-Methylenebisacrylamide (Sigma-Aldrich, St. Louis, MO : Cat # M7279-100g) and 1, 2-Bis(triethoxysilyl)ethane (Sigma-Aldrich, St. Louis, MO : Cat #

Experimental (cont.)

447250-25mL) were diluted w/w in Methanol (Fischer, Fairlawn, NJ : Cat # A456-4). The resulting solutions were analyzed against a calibration curve made using QC27 solution (Agilent, Santa Clara, CA : Cat # 190065000) and Methanol. Both matrices were analyzed in duplicate and both were spiked to assure analyte recovery in the matrix. A second source QC sample was analyzed to assure calibration accuracy.

The calibration standards were prepared at 0.10, 0.50 and 1.00 ppm and example calibrations as well as spectra are shown in Figure 1.

A methanol solution containing 10ppb of all analytes was analyzed ten times and MDLs were calculated for the analytes based on 3 times the standard deviation of the ten replicate readings. The results are shown in Table 2. The 2nd source QC and spiked sample results for the crosslinkers are shown to the right in Table 3.

MDLs in neat Methanol

Element/l	MDL (ppm)	Element/l	MDL (ppm)
Ag 328.068 nm	0.0010	Mg 279.553 nm	0.0008
Al 167.019 nm	0.0029	Mn 259.372 nm	0.0005
As 188.980 nm	0.0051	Mn 257.610 nm	0.0006
B 249.772 nm	0.0053	Mn 294.921 nm	0.0004
Ba 493.408 nm	0.0004	Mo 202.032 nm	0.0019
Be 313.107 nm	0.0004	Mo 204.598 nm	0.0036
Ca 317.933 nm	0.0057	Mo 281.615 nm	0.0009
Ca 393.366 nm	0.0017	Na 588.995 nm	0.0216
Ca 396.847 nm	0.0018	Ni 231.604 nm	0.0021
Ca 422.673 nm	0.0024	Pb 220.353 nm	0.0042
Cd 214.439 nm	0.0008	Sb 231.146 nm	0.0012
Co 238.892 nm	0.0006	Se 196.026 nm	0.0212
Cr 267.716 nm	0.0005	Sr 407.771 nm	0.0002
Cu 324.754 nm	0.0010	Ti 334.941 nm	0.0002
Cu 327.395 nm	0.0010	Tl 276.789 nm	0.0056
Fe 259.940 nm	0.0010	V 292.401 nm	0.0021
K 766.491 nm	0.0737	Zn 206.200 nm	0.0028

Table 2 – Calculated MDLs in Neat Methanol

QC & Matrix Spikes in neat Methanol

Solution Label	Spike (ppb)	MBA %Recovery	BTE %Recovery	ICV/CCV Conc (ppm)	ICV/CCV Reading	% Recovery
Ag 328.068	100	39%	23%	0.500	0.478	96%
Al 167.019	100	94%	90%	0.500	0.502	100%
Ba 493.408	100	96%	93%	0.500	0.501	100%
Be 313.107	100	95%	92%	0.500	0.494	99%
Ca 396.847	100	93%	94%	0.500	0.506	101%
Cd 214.439	100	90%	85%	0.500	0.492	98%
Co 238.892	100	97%	91%	0.500	0.491	98%
Cr 267.716	100	94%	88%	0.500	0.492	98%
Cu 324.754	100	99%	102%	0.500	0.497	99%
Fe 259.940	100	92%	91%	0.500	0.495	99%
K 766.491	100	100%	101%	0.500	0.503	101%
Mg 279.553	100	92%	92%	0.500	0.504	101%
Mn 259.372	100	93%	92%	0.500	0.492	98%
Mo 202.032	100	93%	79%	0.500	0.494	99%
Pb 220.353	100	93%	90%	0.500	0.490	98%
Sb 217.582	100	62%	97%	0.500	0.489	98%
Se 196.026	100	55%	86%	0.500	0.530	106%
Sr 407.771	100	97%	94%	0.500	0.498	100%
Ti 334.941	100	93%	91%	0.500	0.493	99%
Tl 276.789	100	88%	97%	0.500	0.491	98%
V 292.401	100	92%	121%	0.500	0.508	102%
Zn 213.857	100	89%	89%	0.500	0.500	100%

Table 3 – Spike recoveries in Neat Methanol

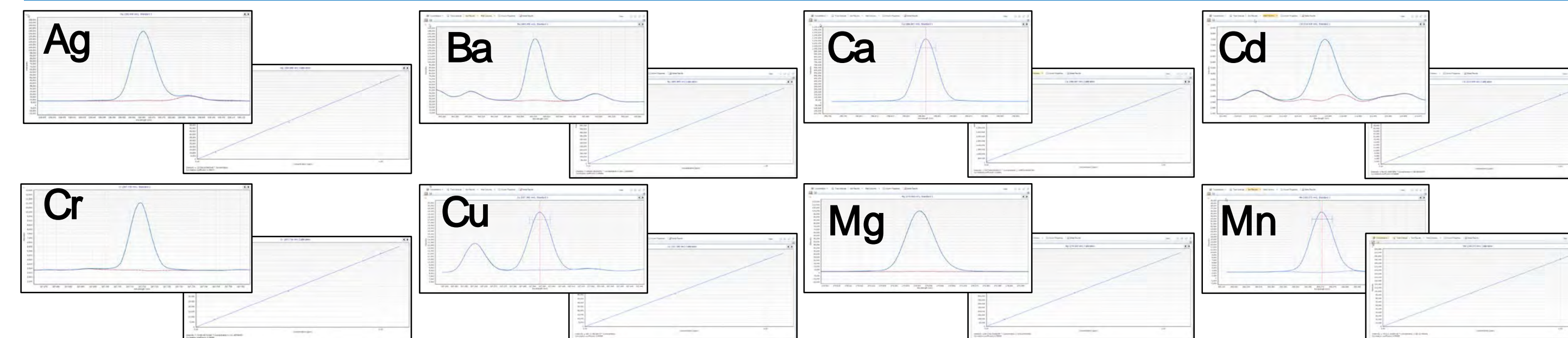## Example Calibrations and 100ppb Spectra in Neat MeOH

Figure 1 – Example Calibration Curves and 100ppb Spectra

ICP-OES Analysis in Chloroform

Calibration blank and standards were prepared by taking a ~1g aliquot of an Organic A21 + K solution (Agilent, Santa Clara, CA: Cat # 5190-8603). Sample introduction consisted of a semi-volatile torch (Agilent; G8010-60233) and an IsoMist Temperature-Controlled Spray Chamber (Agilent; Cat # G8486A #100). Instrument operating conditions are shown in Table 1.

A chloroform solution containing 200ppb of all analytes was analyzed ten times and MDLs were calculated for the analytes based on 3 times the standard deviation of the ten replicate readings. A second source QC sample was analyzed to confirm calibration validity.

The results for the MDL and the QC sample are shown in Table 4.

Solution Label	QC % Recovery	MDL (ppb)
Ca 396.847 nm	101%	2.3
Cr 267.716 nm	98%	1.9
Cu 327.395 nm	103%	1.9
Fe 238.204 nm	97%	2.0
Mg 279.553 nm	101%	1.3
Na 589.592 nm	106%	7.5
Ni 231.604 nm	99%	9.6
Pb 220.353 nm	99%	12.6
V 292.401 nm	99%	2.5
Zn 213.857 nm	101%	1.6

Table 4 – QC Recoveries/MDLs in Chloroform

Conclusion

The Agilent 5110 ICP-OES offers:
- The ability to analyze solvents neat
- High total dissolved solids tolerance (25% TDS) allows for lower dilution factors on dissolved materials
- Part per billion detection limits achievable in numerous solvent matrices