TELEDYNE INSTRUMENTS
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Application Note

Comparative Analysis of Tekmar 3000 and 3100 Purge and Trap Sample Concentrators: Performance Evaluation Between Electroform Nickel and Silcosteel-coated Sample Pathways

By: Glynda Smith

Abstract

The Tekmar 3100 Sample Concentrator represents an improvement to the 3000 Purge and Trap product line. Silcosteel® tubing and Silcosteel-treated sample fittings are used throughout the sample pathway of the 3100. Silcosteel treatment involves a process that shields active metal surfaces. A thin, silicon-based coating is applied to the metal surface, which keeps analytes from adsorbing onto active sites on the metal. As a result, there is enhanced inertness, corrosion resistance, and reduced adsorption. The 3100 Sample Concentrator also has a redesigned valve oven and mount temperature control that improves temperature uniformity of the heated sample pathway. This helps reduce carryover, condensation and adsorption. Prior to the introduction of the 3100 with Silcosteel, the sample pathway consisted of electroform nickel and fittings constructed with electroless nickel plating. Difficulties can occur in the analysis of thermally labile analytes, high boiling compounds, volatile organic sulfur compounds, and some environmental target compounds such as 1,1,2,2-tetrachloroethane. These compounds are targeted for evaluation because they are prone to break down and adsorption onto active metal surfaces. In this paper, the results of a comparison study between samples evaluated using a Silcosteel sample pathway in the 3100 Sample Concentrator and an electroform nickel sample pathway in the 3000 Sample Concentrator will be presented and discussed.

Introduction

The goal of any analytical method is to provide precise, reproducible results. Problems can be encountered if there are sites in the analytical system which permit condensation or adsorption to occur. The incorporation of Silcosteel-treated tubings and fittings in purge and trap systems provides an inert sample pathway that prevents adsorption from occurring. The Tekmar 3100 Sample Concentrator possesses a sample pathway and fittings that are completely shielded with a Silcosteel coating. The Tekmar 3000 Sample Concentrator contains an electroform nickel sample pathway. Over time, difficulties have arisen with the electroform nickel resulting in breakdown and adsorption of particular analytes. For this paper, a comprehensive study is performed on both the Tekmar 3100 and Tekmar 3000 Sample Concentrators and the results are compared.

Experimental

Tables 1 and 2 describe the analytical conditions employed in this study. Method 524.2 Rev. 4 standards were obtained from Restek Corp. (VOA Kit – Cat. #30447).

Line Temperature:	150°C	Trap:	VOCARB 3000
Valve Temperature:	150°C	Desorb Preheat:	245°C
Sample Temperature:	20°C	Desorb Temperature:	250°C
MCS Line Temperature:	50°C	Desorb Time:	4 min.
Purge Time:	11 min.	Bake Temperature:	270°C
Dry Purge Time:	8 min.	Bake Time:	12 min.

Table 1. Purge and Trap Conditions for Tekmar 3000 and 3100 Sample Concentrators

Sales/Support: 800-874-2004 · **Main:** 513-229-7000
4736 Socialville Foster Rd., Mason, OH 45040
www.tekmar.com

Injector:	110°C, Split 30:1
Column:	J&W Scientific, DB-VRX, 60m x 0.25 mm x 1.4 µm
Temperature Program:	45°C (hold 10 min.); Increase to 190°C at 12°C/min and hold at 190°C for 2 minutes. Increase to 225°C at 6°C/min and hold at 225°C for 1 minute.
Carrier:	Helium, at 1.2 mL/min.
Ion Trap Temperature:	150°C
Transfer Line Temperature:	250°C
Electron Multiplier:	1500 volts
Mass Range:	35-260 amu

Table 2. Varian 3800 GC/Saturn 2000 Ion Trap Mass Spectrometer Conditions

Results and Discussion

Figure 1 shows the chromatograms obtained for the 502.2 compound mix run at 10 ppb on the Tekmar 3100 and 3000 sample concentrators. Table 3 lists the results obtained for the compound list on the two instruments.

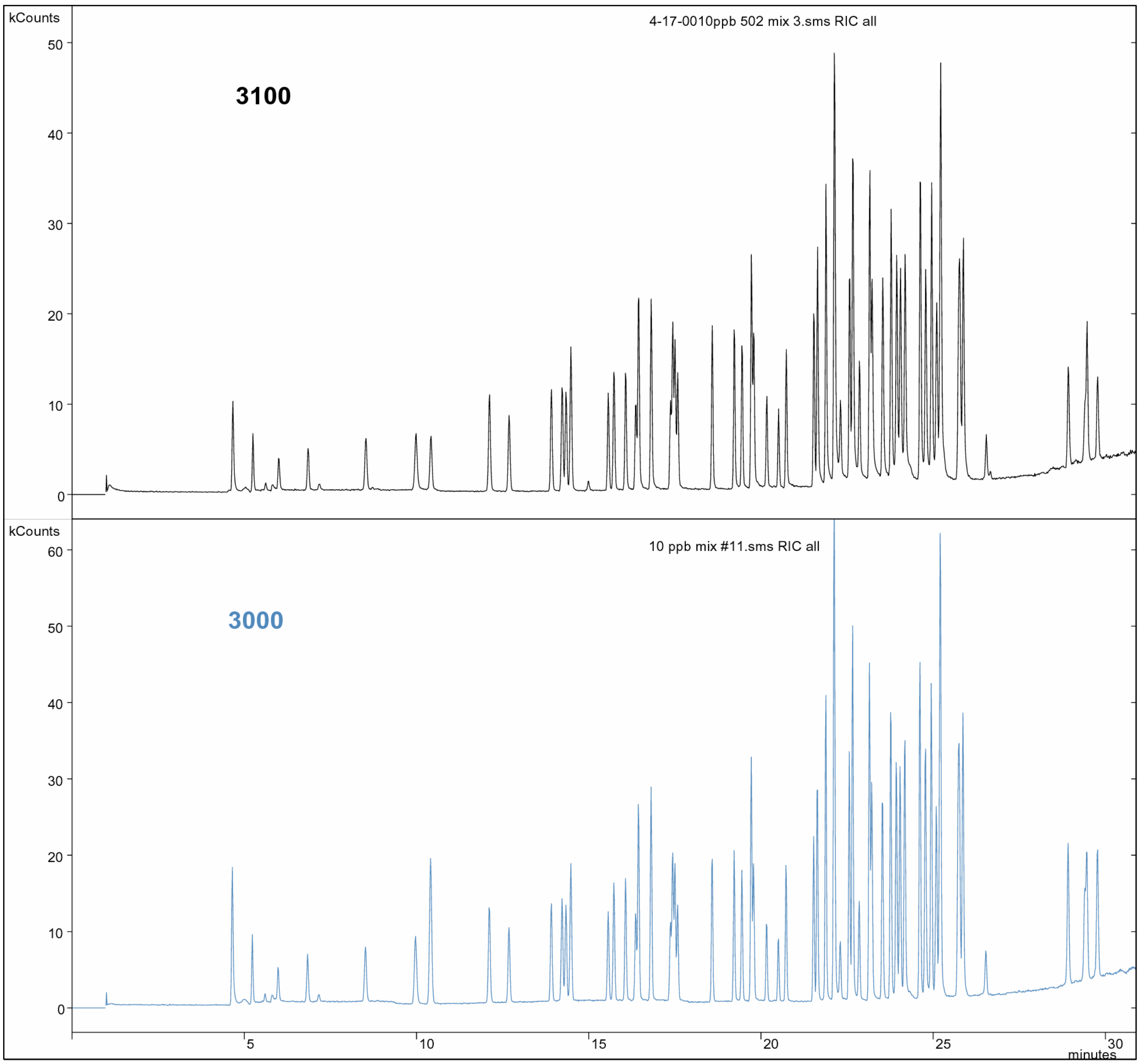

Figure 1. Chromatograms for 502.2 Compound List on 3100 and 3000 Sample Concentrators.

	3000	3100	3100
Compound	**Avg. RF**	**Avg. RF**	**% Change**
Dichlorodifluoromethane	0.202	0.22	+8.18%
Chloromethane	0.035	0.039	+11.42%
Vinyl Chloride	0.173	0.187	+7.49%
Bromomethane	0.249	0.262	+4.96%
Chloroethane	0.04	0.042	+5.00%
Trichlorofluoromethane	0.336	0.359	+6.41%
1,1-Dichloroethene	0.484	0.468	-3.42%
Methylene Chloride	0.663	0.73	+9.18%
trans-1,2-Dichloroethene	0.583	0.611	+4.58%
1,1-Dichloroethane	0.465	0.479	+2.92%
cis-1,2-Dichloroethene	0.557	0.584	+4.62%
Bromochloromethane	0.554	0.601	+7.82%
Chloroform	0.549	0.585	+6.15%
2,2-Dichloropropane	0.781	0.822	+4.99%
1,2-Dichloroethane	0.481	0.507	+5.13%
1,1,1-Trichloroethane	0.649	0.666	+2.55%
1,1-Dichloropropene	0.635	0.643	+1.40%
Carbon Tetrachloride	0.43	0.45	+4.44%
Benzene	1.072	1.085	+1.20%
Dibromomethane	0.371	0.376	1.33%
1,2-Dichloropropane	0.747	0.856	+12.73%
Trichloroethane	0.695	0.682	-1.91%
Bromodichloromethane	0.512	0.591	+13.37%
cis-1,3-Dichloropropene	0.699	0.756	+7.66%
trans-1,3-Dichloropropene	0.696	0.762	+8.66%
1,1,2-Trichloroethane	0.608	0.683	+10.85%
Toluene	1.133	1.078	-4.99%
1,3-Dichloropropane	0.595	0.768	+22.53%
Dibromochloromethane	0.383	0.419	+6.94%
1,2-Dibromoethane	0.308	0.346	+10.98%
Tetrachloroethene	0.638	0.662	+3.62%
1,1,2,2-Tetrachloroethane	0.721	0.788	+8.50%
Chlorobenzene	1.085	1.132	+4.15%
Ethylbenzene	1.399	1.433	+2.37%
m-Xylene & p-Xylene	2.596	2.516	-3.20%
Bromoform	0.327	0.528	+38.07%
Styrene	1.116	1.065	-4.79%
o-Xylene	1.764	1.824	+3.29%
1,2,3-Trichloropropane	0.499	0.679	+26.51%
Isopropyl Benzene	1.52	1.459	-4.28%
Bromofluorobenzene	0.997	1.131	+11.76%
Bromobenzene	1.029	1.086	+5.25%
n-Propylbenzene	1.409	1.387	-1.59%
2-Chlorotoluene	1.225	1.228	+0.24%
4-Chlorotoluene	1.209	1.199	-0.92%
1,3,5-Trimethylbenzene	1.449	1.407	-3.04%
tert-Butyl Benzene	1.649	1.641	-0.47%
1,2,4-Trimethylbenzene	1.324	1.179	-10.95%
sec-Butyl Benzene	1.543	1.533	-0.65%
1,3-Dichlorobenzene	1.009	0.992	-1.71%
p-Isopropyl Toluene	2.637	2.574	-2.45%
1,4-Dichlorobenzene	1.788	1.788	0%
Butyl Benzene	1.469	1.425	-3.00%
1,2-Dibromo-3-Chloropropane	0.227	0.238	+4.62%
1,2,4-Trichlorobenzene	0.792	0.667	-15.78%
Napthalene/Hexachlorobutadiene	1.19	1.159	-2.60%
1,2,3-Trichlorobenzene	0.808	0.648	-19.80%
		Sum Average	**+3.80%**

Table 3. 502.2 Compound List Average Response Factor (RF) Comparison. (For n=16)

The 3100 sample concentrator yielded higher responses for the analytes in the 502.2 compound list, with an overall sum average of +3.80%. 1,1,2,2-Tetrachloroethane (+8.5% change) and bromoform (+38.1% change) are two components in the list that have proven difficult in purge and trap analyses. Both of these analytes exhibit an improved response with the 3100 sample concentrator. The only deviation in the data occurs with the responses of the two trichlorobenzene isomers. An additional study is planned in order to optimize the response of these heavier compounds with the 3100 system.

Method 524.2 Rev. 4 Polar Compounds

Figure 2 shows the chromatographic comparison of the polar compounds added in Revision 4 to Method 524.2. Table 4 lists the results obtained on the two instruments.

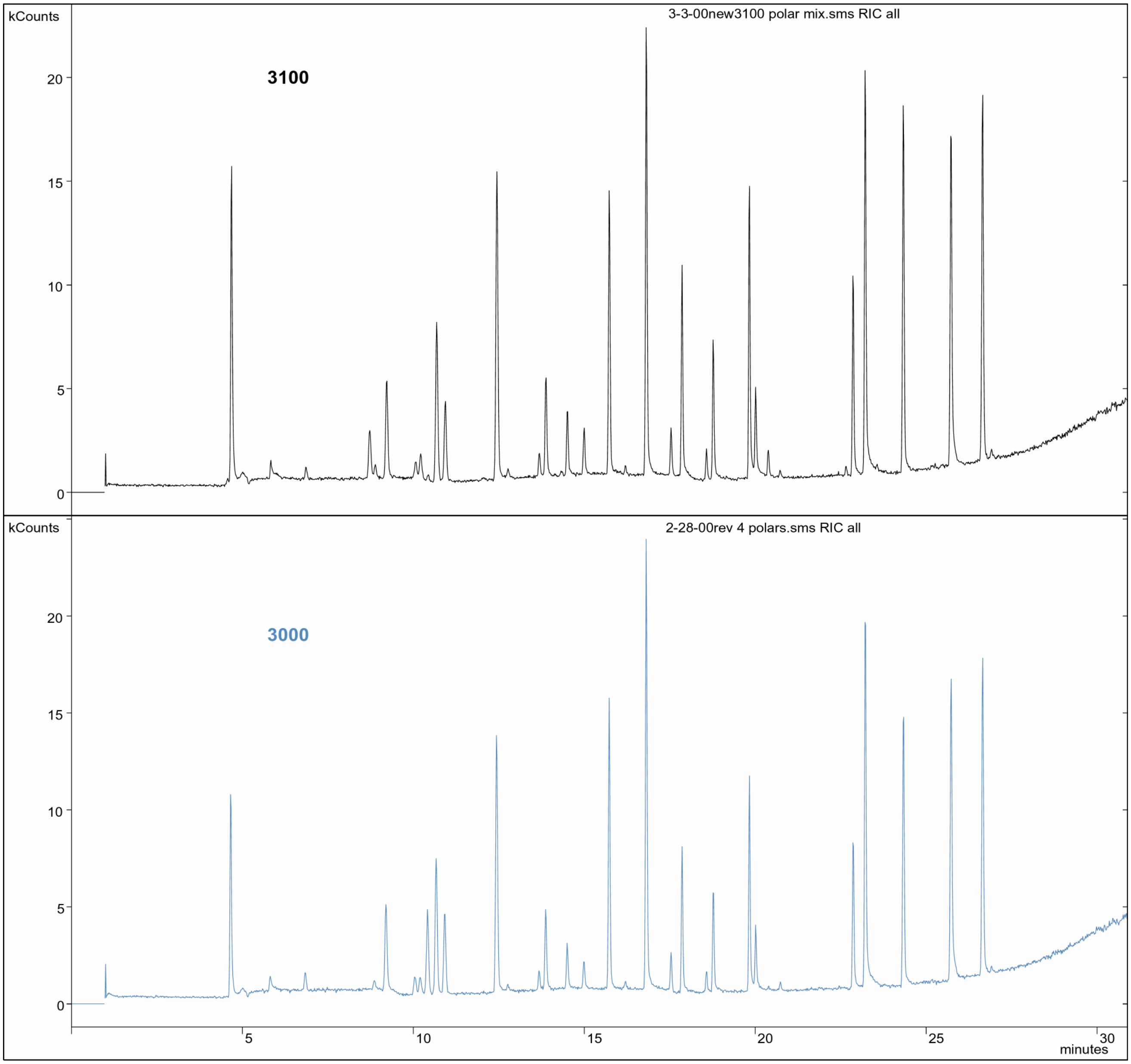

Figure 2. 524.2 Revision 4 Polar Compounds

	3000	3100	3100
Compound	**Avg. RF**	**Avg. RF**	**%Change**
Acetone	0.037	0.043	+16.53%
Diethyl Ether	0.264	0.327	+23.79%
Iodomethane	0.064	0.064	0.00%
Acrylonitrile	0.061	0.078	+27.95%
Allyl Chloride	0.431	0.418	-3.01%
Carbon Disulfide	0.229	0.478	+109.1%
t-Butyl Methyl Ether	0.68	0.826	+21.41%
Propionitrile	0.017	0.027	+54.90%
2-Butanone	0.053	0.059	+10.16%
Methacrylonitrile	0.195	0.231	+18.75%
Methyl Acrylate	0.112	0.138	+23.46%
Tetrahydrofuran	0.076	0.108	+42.57%
1-Chlorobutane	0.601	0.698	+16.26%
Chloroactonitrile	NR	0.016	N/A
2-Nitropropane	0.084	0.094	+11.66%
Methyl Methacrylate	0.31	0.385	+24.22
1,1-Dichloropropanone	0.047	0.057	+20.38%
4-Methyl-2-Pentanone	0.226	0.274	+21.15%
Ethyl Methacrylate	0.434	0.551	+26.90%
2-Hexanone	0.137	0.183	+33.19%
trans-1,4-Dichloro-2-butene	0.311	0.387	+24.49%
Pentachloroethane	0.66	0.761	+15.45%
Hexachloroethane	0.735	0.846	+15.15%
Nitrobenzene	NR	0.025	N/A
		Sum Avg. Change	**+25.20%**

Table 4. 524.2 Rev. 4 Polar Compounds – Average Response Factor (RF) Comparison. (For n=7)

There is a significant increase in the overall response for the polar compounds with the Silcosteel-coated sample pathway. The sum average for the 3100 sample concentrator relative to the 3000 is greater than 25%.

The Rev. 4 polar compounds were also run on a 3000 sample concentrator that was modified with aged nickel tubing. Figure 3 shows the overlaid chromatograms obtained for the 3000 with new nickel tubing and the 3000 with aged nickel tubing.

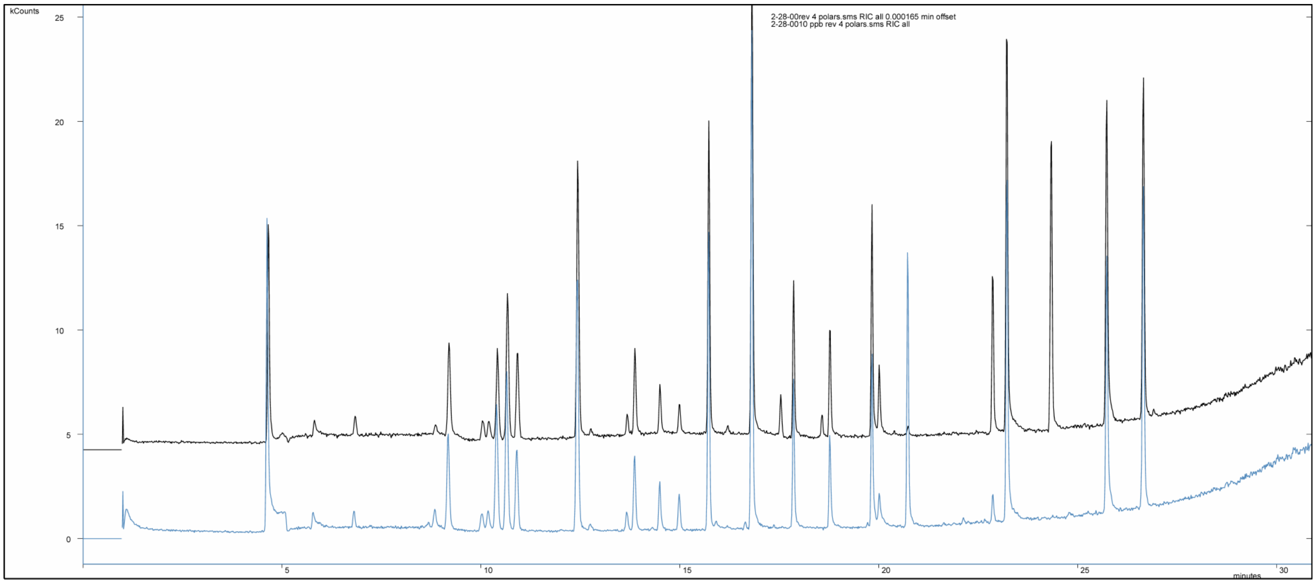

Figure 3. 524.2 Rev. 4 Polar Compounds Overlaid Chromatograms – 3000 with New Nickel Tubing (Black) and 3000 Fitted with Aged Nickel Tubing (Blue)

In comparison with the chromatograms and data shown in Figure 2 and Table 4, the average response factors obtained with the old nickel tubing are even lower than those determined for the 3000 fitted with new nickel tubing. Four of the compounds – methyl acrylate (14.5 min.), 2-nitropropane (17.5 min.), 1,1-dichloropropanone (18.6 min.), and pentachloroethane (24.3 min.) – completely disappeared on the aged tubing. Silcosteel has excellent corrosion resistance and this may be the reason the same aging process is not observed.

Analysis of Sulfur Compounds

A mixture of sulfur compounds at a level of 20 ppb was analyzed on both the 3000 and 3100 sample concentrators. Figure 4 shows the chromatograms that were obtained.

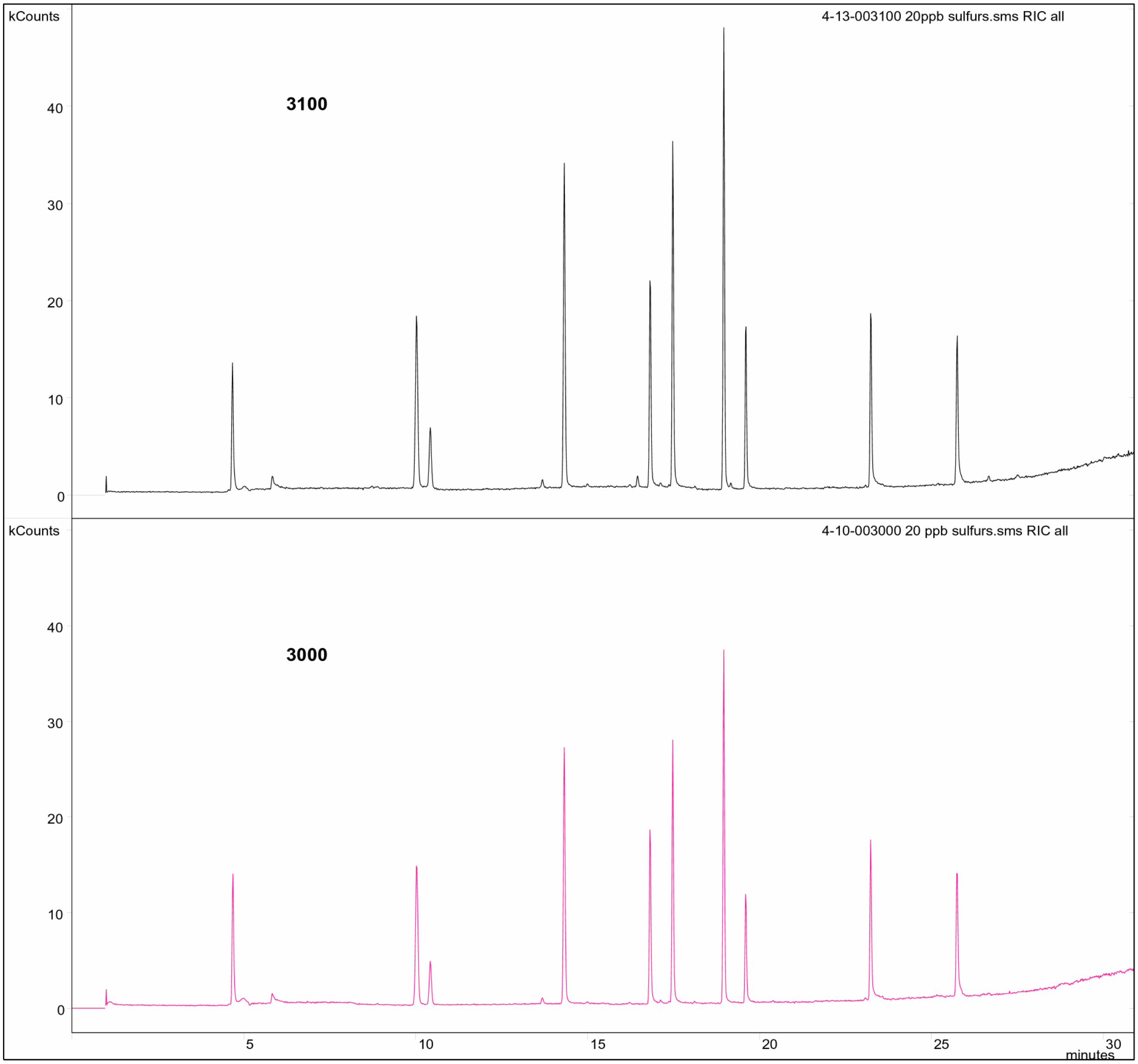

Figure 4. 20 ppb Sulfur Mix Chromatograms

Sulfur standards were obtained from Aldrich Chemical Company. The primary standards were prepared in methanol from the neat liquids. Working standards were prepared in water for analysis on the purge and trap systems. The sulfur mixture contained dimethyl sulfide, ethyl methyl sulfide, ethyl sulfide, dimethyl disulfide, ethyl thioacetate, fluorobenzene (internal standard), 4-bromofluorobenzene (surrogate), and 1,2-dichlorobenzene-d4 (surrogate).

Table 5 lists the average response factor comparison between the two instruments for the sulfur compounds.

	3000	3100	3100
Compound	**Avg. RF**	**Avg. RF**	**% Change**
Dimethyl Sulfide	0.574	0.571	-0.50%
Ethyl Methyl Sulfide	0.705	0.78	+10.64%
Ethyl Sulfide	0.687	0.734	+6.84%
Dimethyl Disulfide	0.872	0.915	+4.93%
Ethyl Thioacetate	0.281	0.367	+30.60%
		Sum Average	**+10.50%**

Table 5. Average Response Factor (RF) Comparison for Sulfur Compounds. (For n=3)

Again, a significant increase in response is obtained with the 3100 sample concentrator relative to the 3000. Figure 5 shows the chromatogram for the same sulfur mix run on a 3000 sample concentrator modified with aged nickel.

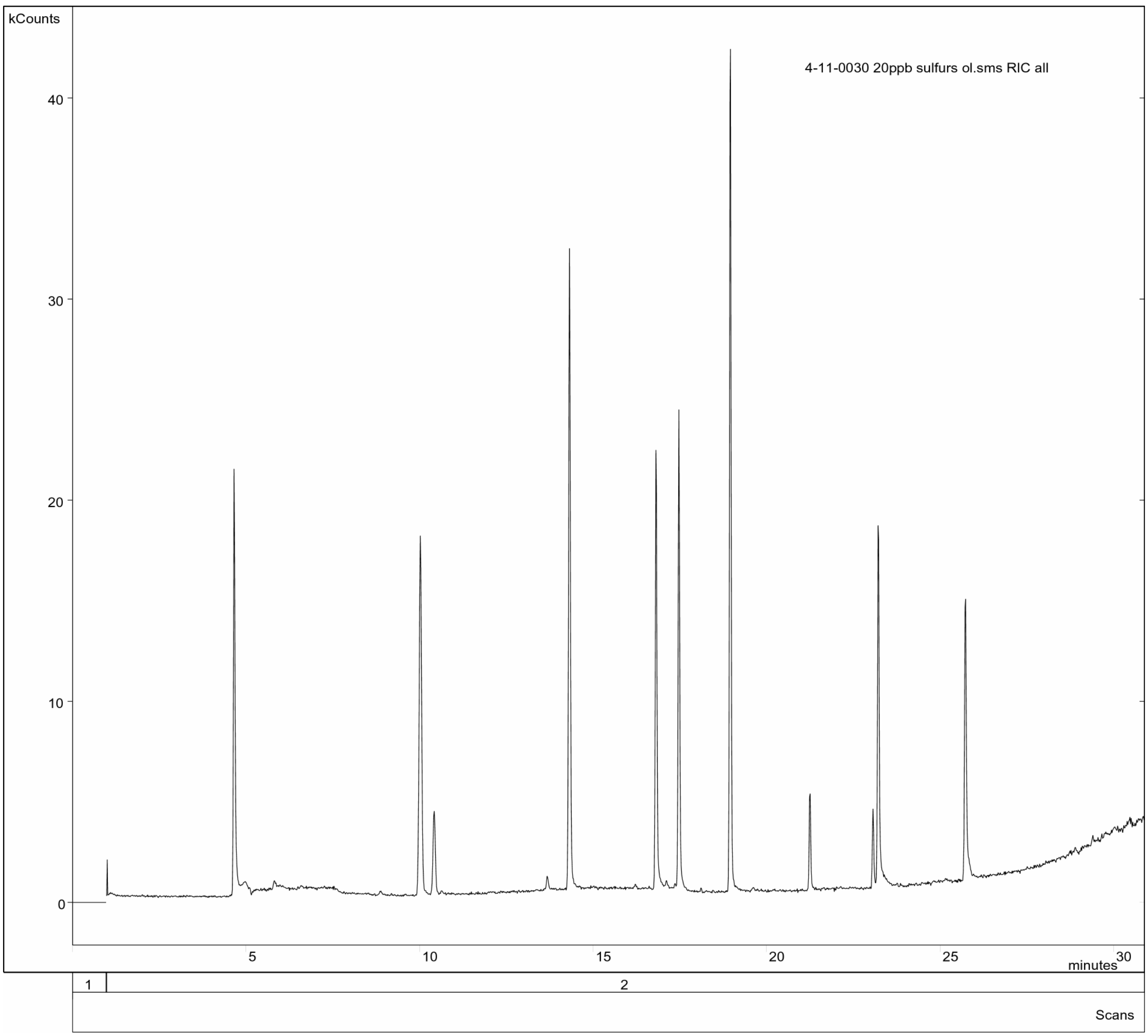

Figure 5. 20 ppb Sulfur Mix Run on a 3000 Sample Concentrator Fitted with Aged Nickel Tubing

With the aged nickel tubing, ethyl thioacetate (19.6 min.) disappears completely. Ethyl sulfide (17.5 min.) shows a reduced response while methyl ethyl disulfide (21.2 min.) and diethyl disulfide (23.1 min.) appear. These new components may be the result of catalysis occurring in the presence of an active metal surface.

Conclusions

The Tekmar 3000 Sample Concentrator with new nickel tubing performs well in all of the evaluations performed in this experiment. As nickel ages, however, the possibility for adsorptive losses on the metal surface increases. This aging may result from the hydrochloric acid that many samples are preserved with. The Silcosteel coating shows greater corrosion resistance than electroform nickel. When the 3000 is compared with the Tekmar 3100 Sample Concentrator which possesses a complete Silcosteel sample pathway and improved temperature uniformity, the 3100 outperforms the 3000. Overall, the average response factors for a large number of the analytes in the 502.2 and 524.2 Rev. 4 compounds lists increase when they are evaluated with the Tekmar 3100 Sample Concentrator.

An additional study is planned to follow-up on this work to examine whether improvements can be made by varying the mount temperatures and other purge and trap parameters in order to optimize analyte responses.