Aluminum and gold-plated aluminum high-pressure mass spectrometer sources

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Aluminum and Gold-Plated-Aluminum High-Pressure Mass Spectrometer Sources

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A high-pressure mass spectrometer source constructed of aluminum and plated with gold may be a viable alternative to the widely used stainless steel construction. Source blocks which take days to machine from stainless steel can be machined from aluminum in hours. This has obvious cost advantages and makes systematic design modifications more feasible. Vapor deposition of gold onto the interior surfaces of the aluminum source gives a clean, nonreactive, highly conductive surface.

EXPERIMENTAL SECTION

Figure 1 shows the stacked ring construction of the source used in these experiments. The design is similar to one that has been reported previously (*1*). The stack is held tightly together with four 6-40 rods. This construction provides design flexibility and allows the ion path length to be varied while other source parameters are held constant. The Teflon spacers make seals sufficiently tight that no problems were observed in reaching chemical ionization (CI) pressures of 0.2–1 torr. The usable temperature range of the source is limited by the Teflon which begins to soften and outgas between 200 and 250 °C. The ion path lengths were 0.5–1.5 cm in these experiments. The relatively small lateral cross section and orthogonal geometry ensure a relatively well-defined ion path length.

The source rings were constructed of 6061-T4 aluminum. The interior surfaces were cleaned with an abrasive pad and rinsed with toluene just prior to gold plating. An approximately 100-nm layer of gold was vapor deposited onto the inside surfaces of all aluminum parts from a tungsten hot zone dimple boat (R. D. Mathis Co. #S8A-.005W) using a Veeco VE-7700 vacuum deposition apparatus with a Veeco ED-200 Evapatrol Controller. The interiors of the source rings were coated by supporting the boat inside the rings on brass rods. It was possible to coat the entire inner surface of a ring with a single deposition, perhaps because the gold crept to the outside of the tungsten boat. The nominal thickness of the gold layer was monitored with an Inficon XTM quartz crystal deposition monitor. No effort was made to study effects of layer thickness. The gold layer adheres moderately well to the aluminum surface but cannot be cleaned by the usual methods. The gold layer has been replaced approximately every 4 months. There have been no problems with the gold migrating onto insulated source parts. The mass spectrometer used in these experiments is a DuPont/CEC 21-110B mass spectrometer that has been modified extensively for high-pressure operation (*2*).

RESULTS AND DISCUSSION

Initial experiments were performed with an unplated aluminum source. High-pressure mass spectra (above about 0.1 torr) obtained with this source were essentially identical with spectra obtained with other sources. Methane gave predominantly CH_5^+ and $C_2H_5^+$ in a ratio of about 1 to 0.8. Methane chemical ionization (CH_4 CI) spectra of organic compounds obtained under these conditions were also very similar to spectra obtained with a stainless steel source. The unplated Al source is suitable for general CI work.

Table I. CH_4 CI Spectra of *n*-Butyl Propanoate[a]

		% abundance[b]	
species	*m/z*	Au/Al	stainless steel
$C_4H_9^+$	57	27	23
$C_2H_5CO_2H_2^+$	75	100	100
$(M + C_2H_5 - C_4H_8)^+$	103	18	19
$(M + H)^+$	131	65	66
$(M + C_2H_5)^+$	159	6	5
$(M + C_3H_5)^+$	171	8	9
$(M + C_4H_9)^+$	187	4	5
$(M + H + M)^+$	261	22	24

[a] $P(CH_4) \cong 0.4$ torr; ion path length $\cong 1.2$ cm. [b] Ions less than 5% of base peak not reported.

The field strength within the unplated source was not well-defined. No significant change in the extent of conversion of CI reactions (and hence in the ionic residence time) was observed when the potential difference between the ion exit plate (part d in Fig. I) and the back plate (part a in Fig. I) was changed. No meaningful kinetic data could be obtained. The detectable ion current was stable for long periods of time indicating that there was no buildup and decay of surface charges within the source. The anomalous field strength results may, however, be caused by a steady-state charging of the aluminum oxide layer covering the aluminum surface. The gold layer was applied to eliminate this effect.

With the gold-plated source, the distribution of ion intensities in the high-pressure mass spectrum of methane was that obtained previously. The CH_4 CI spectra of several simple organic compounds were essentially the same as spectra obtained with a stainless steel source. Table I shows typical data for *n*-butyl propanoate obtained with the Au/Al source and a stainless steel source with similar geometry. The abundant ion at *m/z* = 261 and the less abundant ion at *m/z* = 187 are products of sample ion/sample molecule reactions resulting from the large extent of conversion in the long path sources. Under these conditions of relatively high methane pressure and relatively low field strength within the source, the residence times of reagent ions depend on their drift velocities and the length of the source. The residence time, and consequently the extent of the CI reactions, can be increased by increasing the source path length. However, with this simple source design the detected ion current decreases approximately as the square of the source length. A not yet optimized path length will give maximum sensitivity for analysis.

The field strength in the Au/Al source appears to be well-defined. Qualitative experiments show a consistent decrease in the extent of reaction with increasing field strength. The rate constants for a few reactions of CH_5^+ using reaction
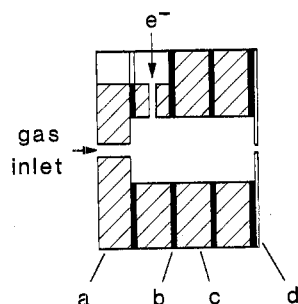
Figure 1. Cut away view of stacked ring source construction: (a) back plate; (b) Teflon spacer; (c) source ring; (d) ion exit plate.

times calculated from literature values of the ionic mobility (*3*) are in reasonable agreement with previously reported range of values. Alternatively, one may use the known rate constants and drift times to calculate the concentration of samples in the source without specific calibration factors. Estimates of small concentrations of ethane in methane using this tech-

nique, for example, agree within ±25% of the values obtained by volumetric dilution.

No unusual surface effects have been observed with the Au/Al source. Very sensitive studies of surface catalyzed radical combination reactions under CI conditions showed the Au/Al surface to be somewhat less reactive than a stainless steel surface (*4*).

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Autozeroing Microcomputerized Boxcar Integrator

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Transient recorders and signal averagers are frequently indispensable data acquisition tools. For slow signals there are many excellent commercial recorders and averagers. For faster signals (<1 μs) the most common solution is a boxcar integrator or a sampling-oscilloscope (SO) based boxcar integrator. Minicomputer (*1*) or microcomputer (*2*) controlled SO boxcars circumvent the drift, inflexibility, and inefficient averaging of earlier analog boxcars. For example, our powerful 8-bit microcomputer based system was programmed in machine language and provided signal averaging, subtraction or addition of transients, and oscilloscope or recorder display of recorded transients; risetime was ≤ 0.35 ns (*2*).

We have greatly enhanced our earlier high-speed SO based system. We added a computer which runs a high-level language permitting on-line data reduction and simpler software modification. In many applications of boxcars, averaging is frequently carried out over extended periods. Therefore, base line drift and modulation of the signal due to source fluctuations during the averaging will degrade the quality of the final results. In extreme cases all useful information will be lost. We developed an autozeroing system for real time base line correction and an averaging algorithm which minimizes the effect of source fluctuations on the shape of averaged wave forms. We describe these system enhancements and performance.

Commercially available boxcars, when suitably interfaced to a computer, are capable of all of the above operations and may even use some of our circuitry. The SO based boxcars are, however, less expensive than equivalent commercial systems, and the SO can also be used as a conventional high speed oscilloscope.

EXPERIMENTAL SECTION

The theory and computer control of SO's have been discussed earlier (*1–3*), and we repeat only that information necessary to understand our circuit. Computer control of the SO requires three

connections between the computer and the SO. These are (1) the signal ready line (SR) from the SO which indicates when a new datum point has been acquired and is ready for digitization, (2) the analog output from the SO which corresponds to the analog voltage of the input signal at the sampled point, (3) the analog external sweep signal to the SO which sets the delay time between triggering of the SO and acquisition of the sampled point. By sequentially delaying the time at which the SO samples it, the transient is built up as a discrete point representation. A stable, repetitive transient is required, but SO's are much faster than conventional oscilloscopes.

In the computerized SO the computer controls the sampling delay by setting the sweep voltage with a digital to analog converter (DAC). Data amplitudes are read with an analog to digital converter (ADC). Synchronization is through the SR line.

System and Autozero Function. Figure 1 is a schematic diagram of the complete system incorporated into our laser nanosecond decay time apparatus. Extension to other instruments is straightforward. The SO and the necessary modifications are described elsewhere (*2*). The signal source is a photomultiplier (PMT) which monitors the luminescence decay of a laser excited sample. The laser is free running and a trigger PMT monitoring the laser beam triggers the system.

Data acquisition from the SO is initiated by a pulse from a trigger PMT which monitors the laser beam. This pulse triggers the SO which samples the signal at the point on the time axis dictated by the external sweep voltage (set by the DAC in the computer interface, CI). Once the signal output stabilizes, the SO pulses the SR line indicating the presence of a new datum point. The signal is amplified by the signal conditioner, SC, and digitized by the interface.

Autozeroing is implemented as follows: (1) after the datum point is collected the computer waits for the transient to decay back to the base line; (2) The computer then issues a command to the trigger generator, TG, which retriggers the SO. The selected delay is long enough so that the signal wave form has decayed to the background level but short enough so that base line drift is negligible. (3) When the SO has acquired this point it pulses the SR line, and the computer digitizes the new datum point which