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the quenching phenomena which lead to interference in fluorescence spectroscopy will not affect the Raman intensities. Extension of this work to low temperature should result in even higher selectivities and sensitivities. It is likely that UV resonance Raman spectroscopy will become a powerful new technique for characterizing complex samples containing chromophores absorbing in the UV spectral region.

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Use of Teflon Components in Photochemical Reactors

Sir: In recent years, several workers (1, 2) have advocated the use of Teflon reaction coils in postcolumn photochemical reaction detectors for high-performance liquid chromatography (HPLC). The major advantages of Teflon over quartz are that it is less fragile and more readily manipulated. Teflon FEP transmits UV light at wavelengths above 240 nm although the transmittance falls below 280 nm (at 260 nm, it is one-tenth of that of quartz). Its efficiency at low wavelengths is believed to be enhanced by diffuse radiation transfer and internal reflectance (1).

Teflon is also a recommended material for use in trace metal studies where the hydrophobic surface is less likely to result in adsorptive losses and is readily purified of trace metal contaminants by acid washing. The latter feature makes Teflon bottles an attractive alternative to quartz tubes for the UV irradiation of natural water samples. This treatment is of value in trace metal speciation studies where irradiation at natural pH values releases organically bound metals (3). The application to aluminium speciation is of particular concern since the possibility of adsorptive losses of released aluminium, as both hydrolyzed and polymerized species, is high at natural pH values.

To examine this, samples of seawater and freshwater containing aluminium complexes were irradiated in both batch and continuous flow reactors. The former used Teflon FEP bottles (Nalgene Labware) of 60-mL capacity, in the 550-W irradiation rig described previously (4). Coil irradiations were carried out using an 8-ft length of Teflon FEP tubing ($1/16$ in. o.d. \times 0.012 in. i.d.) coiled around a Pen-Ray Model 3SC-9 UV lamp (Ultra-Violet Products Inc., CA) enclosed in an aluminium block. Solutions were pumped through the coil at variable flow rates. Teflon bottles and tubing were cleaned before use by soaking overnight in dilute nitric acid followed by rinsing with distilled water and sample.

Analysis of the batch irradiated samples showed more reactive aluminium in solution in samples contained in Teflon bottles than those in quartz. Closer examination revealed that this was due to a decrease in pH of the solutions in Teflon to 3.5 and soluble fluoride ion concentrations as high as 20 mg L⁻¹ (Table I), which apparently resulted from photode-

composition of the Teflon surface. The effect of irradiation time is shown in Table I. Fluoride release also occurred from acidified samples. The same containers are used for six subsequent runs with similar results being obtained.

The slow initial increase in fluoride ion with time suggested a reaction temperature effect. The temperature of the sample in the Teflon bottle reached 55 °C, although the outer surface of the bottle was significantly hotter, and this temperature would only be reached after irradiation for about 0.5–1 h. When placed in a water-jacketed quartz container, the sample in the bottle was kept at an ambient temperature of 30 °C although the incident radiation was reduced. Under these conditions the rate of formation of fluoride decreased significantly with 0.9 mg L⁻¹ being detected after a 4-h irradiation. Even so, this concentration is sufficient to complex aluminium at microgram per liter concentrations.

When the coil reactor was used, it was not possible to cool the lamp and the temperature on the outside of the Teflon tubing reached 48 °C, as specified by the manufacturer. When the solution flow rate was lowered, the contact time of the solution with the surface increased and raised the temperature of the solution. Fluoride release approximated a linear function of solution residence time in the coil. For flow rates of 0.5 and 1.0 mL min⁻¹, respectively, effluent fluoride concentrations of 12 and 5 mg L⁻¹ were detected. For effective photodecomposition to occur, recommended flow rates for postcolumn photochemical reactors are between 0.5 and 1.0 mL min⁻¹ (2, 5).

The use of Teflon coils in photoconductivity detectors should therefore result in a high background conductance which would significantly limit the sensitivity of the detector. For example, for a 350-ng injection of 2,3,7,8-tetrachlorodioxin, assuming 1% photolysis as approximated by Popovich et al. (5) for a quartz reactor, the solution chloride ion concentration reaching the conductance cell would be in the range 10–20 μ g L⁻¹ compared to a background fluoride ion concentration of 5–10 mg L⁻¹.

Workers contemplating the use of Teflon components in photochemical reactors are therefore cautioned to consider whether in their particular application fluoride and hydrogen

Table I. Fluoride and Hydrogen Ion Release from Water Samples Irradiated in Teflon Bottles

time, h	seawater		freshwater		distilled water		acidified fresh- water
	pH	F ⁻ , mg L ⁻¹	pH	F ⁻ , mg L ⁻¹	pH	F ⁻ , mg L ⁻¹	F ⁻ , mg L ⁻¹
0	7.5	<0.1	7.0	0.2	5.5	<0.1	0.2
0.5	7.3	0.1	7.0	0.3	4.5	0.4	0.3
1.0	7.0	0.3	6.9	0.4	4.1	0.8	0.6
2.0	7.0	1.9	6.8	1.4	3.8	2.8	1.8
3.0	6.8	3.4	6.2	3.1	3.6	6.0	3.6
4.0	5.8	11.9	5.7	8.2	3.5	9.1	7.8
5.0	3.7	19.8	4.6	10.1	3.4	13.0	10.8
6.0	3.5	25.5	3.8	13.8	3.2	17.0	17.5

ion release can be tolerated in the concentrations described.

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Registry No. Teflon, 9002-84-0; fluoride, 16984-48-8; hydrogen ion, 12408-02-5; water, 7732-18-5.

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Resolution Requirements for Middle-Molecule Mass Spectrometry

Sir: Coincident advances in ionization techniques, analyzers, and detection systems have recently made feasible the analysis by mass spectrometry of compounds in the mass range 5000-10 000. Such determinations are presently made at resolutions varying from 500 to 80 000. As new instruments are developed to extend this mass range further, the question of resolution should be addressed, as it affects cost, sensitivity, and, most importantly, the information content of the spectrum. We wish here to advance one observation on resolution.

It has been noted by us and others that organic molecular and fragment ions in this mass range comprise multiple isotopic species of different masses, the most abundant of which carry several ¹³C atoms (1-6). In the protonated molecular ion cluster for porcine insulin, for example, 12 peaks are detected at unit resolution between m/z 5774.6 (the monoisotopic mass) and 5785.6 (6) (Figure 1). Molecular formulas for peptides, nucleotides, and other polyheteroatomic species in this mass range provide sufficient abundances of ²H, ¹⁵N, ¹⁸O, etc. that each of the unit mass peaks in the isotope cluster will, in fact, represent numerous isobars. This will be true when an ionization technique such as FAB or SIMS is used, even for the peak at the monoisotopic mass, because loss of one or more hydrogen atoms, reported by many workers (7-9) and observed as peaks below m/z 5774.6 in Figure 1, will carry isobaric multiplicity to lower masses in the isotope cluster.

Mass spectrometry has been used for many years to provide information on the elemental composition of a molecular or fragment ion (10, 11). An accurate mass measurement requires sufficient resolution of isobars. Furthermore, the lower relative intensity or uncertainty in the identity of the monoisotopic mass may necessitate such measurements for one of the more

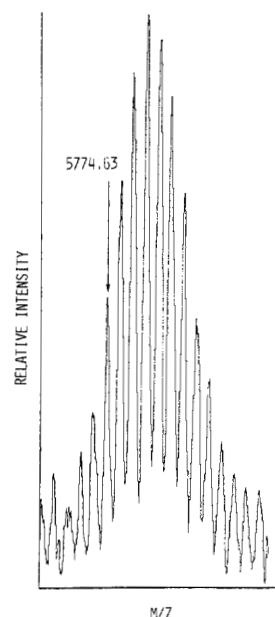


Figure 1. Protonated molecular ion cluster for porcine insulin obtained at unit resolution (adapted from ref 6). The monoisotopic mass is m/z 5774.6. Mass assignments were made by voltage scanning using CsI clusters for calibration.

intense peaks. Figure 2 shows the separation at three resolutions of the eight most abundant isobars among the more than 20 isobaric species which contribute to the peak at m/z 5776.6 in the protonated molecular ion group of porcine in-