



Troubleshooting

Guest Authors

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**How can internal
LC surfaces be made
less reactive?**

John W. Dolan
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Stainless Steel Surfaces in LC Systems, Part II — Passivation and Practical Recommendations

In the first part (1) of this series, we described the structure of stainless steel. We noted that surfaces that many of us consider to be inert actually are subject to significant corrosion and erosion processes under certain conditions. This month, the discussion continues and includes some practical guidelines for stabilizing the stainless steel surfaces of liquid chromatography (LC) systems.

Nitric Acid and Stainless Steel Surfaces

Nitric acid is a widely used reagent for cleaning and passivating stainless steel surfaces because it is a strong acid and a strong oxidizing agent with special concentration-dependent properties. At concentrations less than 10% (1.5 mol/L), nearly all of the nitric acid is in ionic form ($H^+ + NO_3^-$). As the concentration increases, more of the nitric acid is present in the molecular form (HNO_3):



At a concentration of approximately 50% (7.5 mol/L), roughly one-third of the nitric acid is present in the molecular form (2). Thus, the ratio of the more rapid oxidizing agent (HNO_3) (3) to the *slower* oxidizing agent (NO_3^-) (4) increases by a large factor — approximately 15 — in the 10–50% concentration range (2), which makes 50% nitric acid a much more effective oxidizing agent than 10% nitric acid.

In terms of its place in a Pourbaix diagram (3), the range of concentrations discussed in the preceding paragraph fall in a very narrow band of pH –1 to pH 0. Thus, changing from the so-called lower concentrations (10–30% nitric acid) to higher concentrations (~50%), the difference is only approximately one-half of one pH unit.

The oxide layer formed on a stainless steel surface as a result of a passivation procedure is a defense barrier against attack by aggressive fluids. If the surface–oxide interface region is damaged by corrosion reactions, then drastic measures such as deliberate acid treatment of the surface sometimes can replace the corrosion-damaged region with an intact oxide layer. Obviously, this step should be considered carefully. Manufacturers' manuals and troubleshooting literature recommend the use of "dilute" nitric acid for the cleaning and repassivating of a stainless steel surface (5,6). Chromatographers and maintenance personnel should be advised that dilute nitric acid — that is, a concentration of less than 30% (5 mol/L) — is only weakly oxidizing. It also is quite aggressive; it readily attacks unprotected stainless steel. Concentrations of 40–50% (6–7.5 mol/L) should be at least as effective for removing crud deposits, and they also are effective for repassivating a damaged oxide layer. Thus, unless users have a specific reason for doing otherwise, they should use 50% nitric acid, rather than a more dilute nitric acid solution, for cleaning and passivating stainless steel surfaces. Contact time does not appear to be a limiting factor at this concentration and ambient temperature; the stainless steel will not dissolve.

Working with concentrated nitric acid — any concentration greater than 1 mol/L — requires considerable care. Nitric acid is a very hazardous material, even for well-trained personnel (7). Concentrated nitric acid can rapidly destroy human skin, clothing, notebook paper, and other materials found in laboratories. It also gives off vapors that attack mucous membranes and corrode simple (non-stainless steel) metal surfaces. Dolan and Snyder (6) provided some important procedural suggestions, to which we would add:

- Consider purchasing concentrated nitric acid in 500-mL or 1-L bottles. The larger, 2.5- and 4-L economy sizes are more difficult to handle than the smaller sizes, especially for less-trained personnel.
- Prepare 50% nitric acid (normally a 1:1 dilution) using a beaker with a volume marker instead of a tall volumetric cylinder. Fill the marked beaker to the same mark with distilled water, transfer this water to a larger beaker, fill the beaker with the concentrated nitric acid, and then carefully pour the nitric acid into the larger beaker already containing the water.

LC System Microplumbing

A complete LC system comprises a series of large modules — pump, injector, detector, and data system — connected to other components such as a mobile-phase filter, an in-line filter, a saturator column, a guard column, a separation column, and connection tubing. These smaller components are the open microplumbing of an LC system, and they complete the mobile-phase-sample flow path.

Figure 1 shows a typical isocratic LC system. The mobile-phase flow path begins in the mobile-phase reservoir. Most chromatographers use a large-area solvent filter at this point, although others can make an argument for not using a filter here (6). From the mobile-phase reservoir, the flow path includes a series of transport tubes (A–H) that interconnect the various components. Tube A usually is a large-bore polymeric tube (as large as 1-mm i.d.), and it often is constructed from PTFE, which does not corrode in contact with the

mobile phase. The other pieces of tubing (B–H) almost always are 1.5-mm ($\frac{1}{16}$ -in.) o.d., high pressure–resisting material, usually stainless steel. Connections B, C, and D upstream from the injector have 0.5–0.75 mm (0.02–0.03 in.) inner diameters, and connections E, F, and G between the injector and the detector have 0.25-mm (0.01-in.) or smaller inner diameters. The postdetector tube (H) usually has an inner diameter of 0.25 mm or larger.

The check valve unit of most LC pumps is external to the pump housing because the inlet and outlet valves of this unit must be cleaned periodically and can suffer corrosion and require replacement. The pressure-measuring transducer of the pump may, or may not, be accessible from outside the housing, even though this transducer is particularly susceptible to corrosion with aggressive mobile phases, as Pickering (8) discussed. The saturator column–in-line filter unit is an optional component, and Dolan (9) has discussed its use.

Frits, marked by cross-hatching in Figure 1, are important centers of corrosion. They often are the first stainless steel parts of the LC system to show signs of corrosion.

How Can Corrosion Be Checked?

A typical chromatographer can do little to determine the rate of stainless steel corrosion that is occurring in a system without seeing some signs. Because chromatographers' main concern is the presence of corrosion products such as iron, chromium, or nickel in a liquid chromatograph, they should perform on-line or periodic testing of the flow stream for these products to

obtain a practical indication of the presence of corrosion. We are unaware of any literature reports of this procedure being performed on a routine basis.

An alternative approach that can be implemented by any chromatographer is to look periodically at the top, entrance surface of the preinjector saturator column–in-line filter (Figure 1), the guard column, or the column itself. An off-white color is an indication that something is wrong. A rust color strongly suggests an upstream corrosion problem. Note that particles formed as a result of corrosion may be too large to pass through several of the in-line frits, in which case rust-colored frits probably indicate advanced upstream corrosion.

Replumbing an LC System

Before Problems Appear

The corrosion of stainless steel is an insidious process. It continues to develop even when no external indications are present. Analysts have two approaches for dealing with this invisible but ongoing corrosion: "if it isn't detectable, don't fix it" and "if it's easy to fix, let's do it."

A reasonable strategy for those using the second approach is to replace all the accessible high-pressure tubing and all the frits in a routine manner, such as whenever the pump itself is undergoing routine maintenance (for example, when cleaning check valves or changing pump seals). Replacement items can include new stainless steel tubing and frits, especially if no stainless steel problems had developed previously. For example, replacing tubes B–G (Figure 1) with commercial, precut stainless steel tubes would cost less than \$20, plus the cost of new ferrules or plastic connectors, as needed. Frit replacement would cost \$10–30, depending on whether the frits were mounted in polymeric sealing rings.

When the stainless steel surfaces of an LC system present a significant threat to the quality of the data or to the separated products themselves, chromatographers must consider other materials. Many candidate materials have attractive properties.

Two metallic materials with corrosion resistance better than type 316 stainless steel are titanium and Hastelloy C22, which could replace stainless steel in many cases if appropriate parts made of these materials were available and affordable (10). Several of the most commonly used sizes of frits and connection tubing are available in one or both of these metals. They are affordable — they cost only a few times more than comparable pieces made from

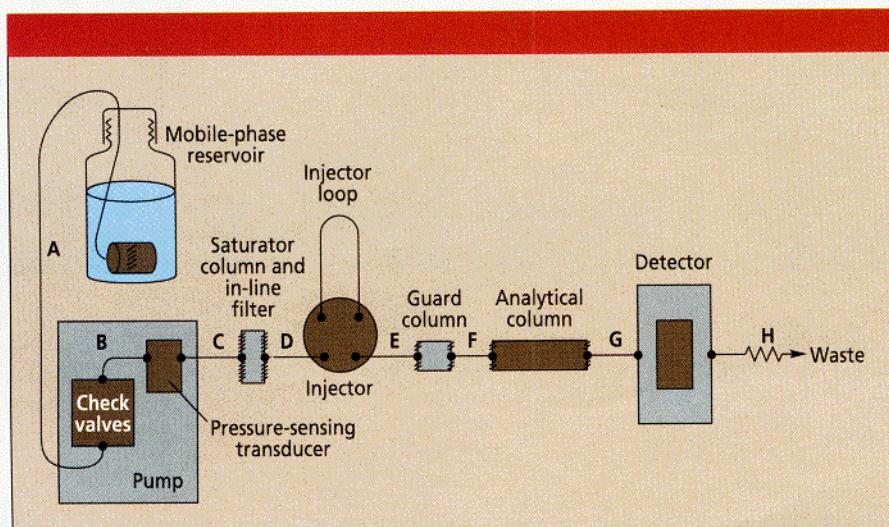


Figure 1: Representation of a typical isocratic LC system. A–H = connection tubing between these components. The hatched markings identify column frits.

stainless steel. However, neither of these metals is inert under all conditions. These materials, like type 316 stainless steel, can be attacked by various acids, bases, and salts, usually under extreme conditions of pH or temperature (11). As for which of these materials is the better choice, until more use experience is reported, we can only note that titanium tubing is more brittle and could be less reliable when connection tubing must be bent sharply (11).

Several organic polymers have favorable surface properties and can displace stainless steel in some corrosion-intensive applications. Poly(etheretherketone) (PEEK) is the best known and most widely used of these new materials. It is widely available in various forms at reasonable cost and has become the material of choice in bio- and ion chromatography applications. However, PEEK and other promising polymeric materials also have limiting properties that may be relevant to use under special LC conditions. PEEK deforms (swells) somewhat in the presence of certain solvents — dimethyl sulfoxide, tetrahydrofuran, and methylene chloride — and its strength diminishes at temperatures higher than 100 °C. It is attacked by concentrated acids and bases but can be used with 25% nitric acid during a brief cleaning procedure (12). PEEK connection tubing is difficult to bend into tight spaces and becomes brittle under some conditions.

Brittleness is a particularly bad property. For example, if a PEEK frit used as the column support (exit) frit were to become brittle, the frit could break, causing loss of packing material, and, probably, stoppage of the mobile-phase flow as the particles moved downstream. It is, presumably, concerns such as this one that have led one supplier to conclude: "We do not recommend PEEK tubing for critical, hazardous, or long-term use, particularly at high pressures" (10).

A few other polymers such as poly(ethyltrifluoroethylene) (Tefzel) and poly(chlorotrifluoroethylene) (Kel-F) also have favorable properties for replacing stainless steel in some LC applications. Their properties are listed in several suppliers' catalogs (10,12).

Finally, we should note several other alternative materials briefly, because they can replace stainless steel and its oxide-coated working surface with non-stainless steel, nonpolymer contact surfaces. Examples of these materials are glass-lined tubing (13), polymer-supported silica tubing

(13), and silica-like coatings bonded onto stainless steel (14). In these cases, corrosion-like effects are not necessarily eliminated; they simply involve other corrosion reactions. For example, silica and glass surfaces are attacked by basic solutions and some acids.

A Corrosion-Hardened LC System

Assembling a new LC system that is resistant to corrosive mobile phases involves selecting from among the various commercially available biocompatible pumps, injectors, and detectors; confirming that the pressure transducer of a pump also is corrosion resistant (or can be made so [8]); and planning, specifying, and confirming the choice of all surfaces along the mobile-phase flow path. At present, the best choice of materials appears to be Hastelloy C22 or titanium tubing for connections before an injection valve and PEEK tubing between an injector and a detector. Hastelloy C22 or titanium tubing also are good choices for all frits and filters in a system.

Recommendations Regarding Corrosion and Passivation

In our opinion, the following steps should be followed to ensure passivation of the surfaces within an LC system:

- Assume all new stainless steel components have clean, well-passivated, fluid contact surfaces.
- Passivate the fluid contact surfaces of all homemade stainless steel components, as well as any stainless steel components such as column blanks that have newly cut or polished surfaces.
- Consider replacing all frits and connection tubing on a regular basis.
- Consider using a degasification system (6) — not only to decrease the possible problems with gas bubbles but also to reduce the concentration of oxygen in the mobile phase. The presence of even low concentrations of oxygen contributes to the stainless steel corrosion process (15), as is indicated by reactions 2 and 3 of Part I of this "LC Troubleshooting" series (1).
- Follow manufacturers' or troubleshooting specialists' recommendations for cleaning or repassivating contact surfaces of pumps, injectors, and detectors. However, use 50% nitric acid, instead of a lower concentration, and use it only as a last resort for the cleaning or repassivation of stainless steel surfaces when replacement is not a viable option.

Conclusion

Well-passivated type 316 stainless steel, as is used in most LC systems, is remarkably resistant to attack by moderately aggressive (for example, 20% nitric acid) to very aggressive (for example, 3% hydrochloric acid or sodium chloride) liquids. This quality can be observed easily in test tube experiments with pieces cut from high-quality column blanks. Chromatographers who use simple mobile phases that have no corrosion-promoting buffers or other salts may never see evidence of corrosion in their LC systems. For those of you who must use these mobile-phase additives, you should remember that corrosion is a continuing process that can occur even under the protective oxide passivation layer, long before visible signs of corrosion appear.

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Editor's note: The guest authors illustrate the importance of preventing corrosion of components in LC systems and provide guidelines for minimizing these problems. However, in private communications, they admit that, for the most part, their experience corresponds to mine — we really don't know the practical impact of stainless steel tubing deterioration on the typical reversed-phase separation method using aqueous-organic mobile phases. I suspect that the problem can be critical for applications such as ion-exchange and ion chromatography or with electrochemical detection when aqueous, buffered, or salt-containing mobile phases are used alone; however, I have experienced no such problems with reversed-phase applications in my laboratory. I would appreciate reader feedback in terms of practical experiences regarding the impact of stainless steel stability on analytical results. Please send written feedback to "LC Troubleshooting," LCGC, 859 Willamette Street, Eugene, OR 97401 or e-mail John.Dolan@LCResources.com. By sharing our collective experiences, perhaps we all can avoid some of the problems pointed out in these two "LC Troubleshooting" columns.

— John W. Dolan

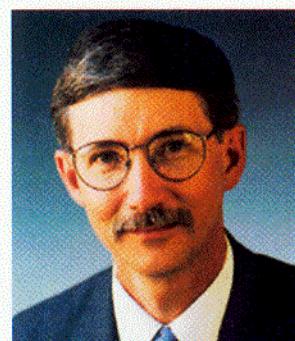
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