

REVIEWS

Deoxygenation of Solutions and Its Analytical Applications

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A representative survey of current methods of solution deoxygenation is presented. Some of the novel, nonconventional methods of degassing are also highlighted. The deoxygenation methodology is examined with special emphasis on luminescence spectroscopy, reductive electrochemical analysis, high-performance liquid chromatography, and liquid chromatography with reductive electrochemical detection. Each of these areas of analytical chemistry is examined with regard to (1) the adverse effects that are caused by the presence of dissolved oxygen in samples and solutions and (2) how the current deoxygenation methodology is applicable to each analytical technique.

The presence of dissolved oxygen causes a variety of undesirable effects for many analytical measurements. Consequently, sensitive, reproducible, and troublefree analysis often requires removal of dissolved oxygen from the analyte matrix prior to analysis of samples. However, because air and, therefore, oxygen, a major constituent of air, are ubiquitous, the removal and exclusion of oxygen from analytical samples and solutions is a formidable task. The amount of oxygen to be removed is dependent on the solvent to be degassed in addition to other factors. Gases are often nonpolar, and therefore, they become increasingly soluble as the solvent polarity decreases. For example, the solubility of oxygen in aqueous solution, expressed as mole fraction of the gas, is 0.2298, whereas the solubility in cyclohexane is 12.48 (1, 2). For solutions at equilibrium with the atmosphere, the dissolved oxygen concentrations are approximately 21% of these values.

Over the years, researchers have used a variety of techniques for deoxygenation of samples and solutions. These techniques vary from rather simple methods, such as purging with an inert gas, to much more elaborate and complicated procedures. In all instances, the objective is to eliminate or considerably reduce (by 95% to >99%) the dissolved oxygen present in analytical samples and solutions. By dissolved oxygen, we refer to those instances in which oxygen is physically incorporated into the solution matrix via solvation either by the solvent alone or by the solvent and other solute molecules (e.g., micelles or cyclodextrins) and not to those cases in which oxygen is chemically bonded to any other species in solution. Although removal of dissolved oxygen from the interior of other solute molecules, such as micelles or cyclodextrins, is more difficult than removal from pure solvent alone, any of the deoxygenation techniques to be discussed are still effective. Those cases in which oxygen is present as a chemically bonded entity in the species of interest and deoxygenation, therefore, necessitates the breaking of chemical bonds, are not within the focus of this paper and, consequently, will not be discussed. This paper will present a survey of the various solution deoxygenation methods that are currently used and examples of the analytical procedures to which these methods are applicable. Several novel methods of sample deoxygenation will

also be discussed (3-8), and some of their specific applications will be highlighted.

Many analytical measurements can be significantly improved with regard to sensitivity and precision when experimentation is done in an oxygen-free environment. For example, the sensitivity of luminescence analysis can be considerably improved with the removal of oxygen, because many fluorescent and phosphorescent compounds are highly susceptible to quenching by molecular oxygen (3, 7-28). Sample deoxygenation is a necessity for analysis by room-temperature phosphorescence (RTP) because the long-lived excited triplet state that produces phosphorescence emission is totally quenched by molecular oxygen in liquid solution (29-40).

Reductive electrochemical analysis also benefits from oxygen removal. High background current and resultant base-line noise are produced by the reduction of residual oxygen present in solutions that are not deoxygenated prior to analysis (41-52). Consequently, without sample deoxygenation, oxygen acts as a major source of interference in polarography, amperometry, and other forms of electrochemical analysis conducted in the reductive mode.

Deaeration of the mobile phase is also routinely used in high-performance liquid chromatography (HPLC) (53-61) because dissolved gases in an HPLC system can cause a variety of analysis problems. Experiments using HPLC with electrochemical detection (LCEC) can be improved by sample deoxygenation and mobile-phase deaeration because of the combined benefits for both HPLC and reductive electrochemical analysis when oxygen is excluded from the analytical working environment (62-67). Spectroscopy, electrochemistry, and chromatography are the major areas of analytical chemistry in which deoxygenation plays an important role. Detailed explanation of other fields is beyond the focus of this paper. However, since the deoxygenation methods outlined below can also be used in other areas of chemistry, the importance of a review study is apparent.

Survey of Deoxygenation Methods

Many approaches have been used for solution deoxygenation. These oxygen elimination procedures vary from those that are relatively simple to implement to those that

are more elaborate. These techniques also differ in that some are used to eliminate all dissolved gases (3, 5, 9–13, 29–32, 41–75) and some are used specifically to control or eliminate dissolved oxygen (4, 6, 76–87). For clarity we will categorize these techniques as vacuum methods, purge methods, and chemical methods. We will also highlight some nonconventional deoxygenation methods.

Vacuum Methods. Vacuum degassing is one of the most frequently used approaches for oxygen removal (54, 58, 60, 70, 71). Decreasing the pressure above the solution allows dissolved gases to be expelled from solution and then removed by the vacuum pump. Some have reported this procedure to be more efficient when repeated in several short cycles as opposed to a single long evacuation period because the greatest reduction in oxygen concentration per unit evacuation time is achieved during the early portion of each evacuation cycle (62, 70). The total amount of oxygen removed by several short cycles is cumulative. Several variations of the vacuum technique have also been described. These include boiling under vacuum (54), "vacuum sublimation" (74), and freeze-pump-thaw techniques (86, 87). In the freeze-pump-thaw procedure, the solution is frozen with liquid nitrogen, the air above the solution is removed with a vacuum pump, and the solution is then allowed to thaw. This procedure is also more efficient when repeated for several cycles (86, 87). By successive freezing and melting of the solution under vacuum, the noncondensable gases can be pumped away.

Purge Methods. Researchers have also used inert gas purging either prior to (63) or following (44, 62, 69) the application of a vacuum to remove dissolved oxygen from solutions. However, one of the most often used deoxygenation procedures is to purge the sample with an inert gas without the supplemental application of a vacuum. This technique, also referred to as sparging or stripping, has been implemented by using nitrogen (14, 29–32, 41–44, 46, 47, 49, 51, 62–68), argon (48, 64, 85), or helium (53–56, 61) as the purge gas. Purging with an inert gas reduces the concentration of dissolved oxygen in the solution in accordance with Henry's law, as shown in eq 1, where P

$$P = kS \quad (1)$$

denotes the pressure of oxygen above the solution, k denotes the Henry's law constant, and S denotes the solubility of oxygen in the solution. The solubility of oxygen in the solution is directly proportional to the partial pressure of oxygen above the solution. Thus, purging reduces the partial pressure of oxygen above the solution, and consequently, the solubility of oxygen in the solution is also reduced. Although purging is usually continued for several minutes (i.e., 15–30 min), in some cases purging time can become lengthy. For example, Lund reports argon purging of a 60:40 methanol-water mixture for 4 h to overnight prior to HPLC analysis with amperometric detection (64). Extensive purging was used because the solubility of oxygen is very high in a methanol-water mixture (64, 88). Baugh reports deoxygenating sulfuric and perchloric acid solutions with nitrogen for 16 h prior to studying the electrochemistry of lead in these media (41–43). Such extensive purging was necessary to minimize trace oxygen reduction currents. Large amounts of gas consumption are also a consideration when using inert gas purging. Purge rates of 5–8 L/min have been reportedly used to obtain adequate deaeration in continuous-flow systems (46, 47).

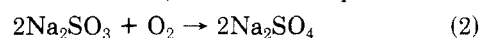
Helium is usually the gas chosen when degassing mobile-phase solutions for HPLC by inert gas purging (53–56). It has been found that helium not only prevents problems in HPLC that are specifically due to the presence of ox-

ygen, but it also eliminates a variety of problems that can arise from the presence of any dissolved gas (56). This is because helium prevents bubble formation and eliminates all other gaseous components from the mobile phase (56). It is postulated that the solubility of helium is low enough to either (1) prevent the manifestation of microbubbles that may be formed or (2) result in very low levels of saturation (56, 89). However, it has also been noted that the low density of helium necessitates special precautions to prevent back-diffusion of air into the solvent bottle during degassing (53, 54). The effects and problems that arise in HPLC due to the presence of dissolved oxygen will be treated later in this discussion.

In samples, such as natural waters, where the pH is determined by volatile components (e.g., CO_2), inert gas purging may produce undesirable changes in the pH (45). Astruc et al. prevented such pH changes by using "isoxic degassing" (45). In this procedure, evolution of CO_2 from the sample was prevented by deoxygenation with a mixture of nitrogen and CO_2 , with the partial pressure of CO_2 adjusted to maintain a constant pH of the natural water sample (45). Polarographic analysis could then be conducted at the natural pH of the waters.

Other degassing procedures include ultrasonification (with evacuation) and the use of reductive oxygen scavenging agents. Ultrasonification, the use of ultrasonic radiation to remove dissolved gases (57), removes gases when sound waves are propagated through a solvent resulting in the formation of cavities or bubbles in the solvent. Any dissolved gases present in the solvent will tend to associate into larger bubbles which then rise to the surface of the solvent. Ultrasonification has been reported to be an "extremely efficient" means of degassing a liquid (57). However, others have found ultrasonic degassing far less successful and deemed it "ineffective" (54). In this case, the concomitant use of a vacuum was not indicated. Perhaps, this procedural difference accounts for the disparity of opinions regarding the efficacy of ultrasonic degassing.

Chemical Methods. Strongly reducing agents, such as chromous sulfate (77–79), vanadous sulfate (76), hydrazine (80–83), and sodium sulfite (81–83) are chemically suitable to function as oxygen scavengers. Prior to the commercial availability of highly pure gases, either chromous sulfate or vanadous sulfate was used routinely to remove oxygen from less pure grades of nitrogen and other gases (76–79). By bubbling the gas to be purified through trains of chromous or vanadous scrubbers, the level of oxygen and other reducible impurities could be adequately decreased. The purified gas could then be used for oxygen removal from solutions or for providing inert atmospheres for reactions. Hydrazine and sodium sulfite are scavengers commonly used for deoxygenation of boiler waters (80–83). Dissolved oxygen is the most common cause of boiler system corrosion (82). Dissolved solids formation is a major factor governing the selection of an oxygen scavenger for boiler applications because large amounts of dissolved solids in boiler systems can cause higher blowdown rates and, consequently, higher fuel and chemical costs (82). Generally, sodium sulfite is used in low-pressure boiler systems (i.e., below 1500 psi) (82, 83). Corrosive hydrogen sulfide and sulfur dioxide can be formed at boiler pressures above 1500 psi. However, sodium sulfite contributes to the total dissolved solids in the boiler water due to the formation of sodium sulfate, as shown in eq 2.



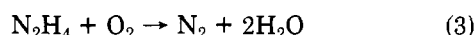
Hydrazine is used in boiler systems above 1500 psi because it does not contribute to the dissolved solids (81, 83).

Table I. Solubility of Oxygen in Liquids at 25 °C and 1 atm of Partial Gas Pressure

solvent	Hildebrand solubility parameter, ^a MPa	solubility, ^b mole fraction × 10 ⁴
water	47.9	0.2298 ^c
methanol	29.6	4.147
ethanol	26.0	5.841
acetone	20.2	8.383
toluene	18.2	9.09
CCl ₄	17.6	12.01
cyclohexane	16.8	12.48
n-hexane	14.9	19.3

^aData compiled from: Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Boca Raton, FL, 1983; pp 142-149. ^bData compiled from: Wilhelm, E.; Battino, R. *Chem. Rev.* 1973, 73, 1-9. ^cData for water from: Wilhelm, E.; Battino, R.; Wilcox, R. *Chem. Rev.* 1977, 77, 219-262.

Hydrazine reacts with dissolved oxygen to form water and nitrogen as shown in eq 3. However, hydrazine has been



classified as a suspect carcinogen by the Occupational Safety and Health Administration (OHSa) and the National Institute for Occupational Safety and Health (NIOSH) (84). Therefore, to eliminate the disadvantages of sulfite use and the hazards of hydrazine use, product research and development has been ongoing to find an oxygen scavenger to replace both compounds (81-83).

Thus, far, this survey of deoxygenation methods has focused on the implementation of conventional, or routinely used, techniques and not their effectiveness relative to one another. The effectiveness of a deoxygenation procedure is dependent on several factors. The solvent being degassed is a major consideration. This is because oxygen solubility generally increases as solvent polarity decreases (56). This trend is evident from the solubility data for oxygen in various solvents shown in Table I. Other considerations include the pressure and temperature at which the experiment is conducted and the solvent composition if mixed solvent systems are used. Depending on the references consulted, opinions differ regarding the relative effectiveness of the various degassing procedures (54, 56, 57). For example, after reviewing the relative efficiency and speed of various degassing techniques, Brown et al. concluded that refluxing was the most effective technique followed by helium purging, vacuum degassing, and ultrasonification, respectively (54), whereas Bakalyar et al. found helium purging of all pure mobile-phase HPLC solvents to be quite effective for their analyses (56). Burke et al. reported that ultrasonic degassing with evacuation for 15 min was equivalent to 6 h of boiling when degassing water (57). When convenience is a major consideration, inert gas purging is usually the method of choice. However, any of the techniques discussed have the potential to sufficiently decrease dissolved oxygen levels if (1) the previously mentioned factors upon which deoxygenation effectiveness depends are taken into consideration when selecting the method and (2) proper analysis procedure and sufficient implementation time are used. Most of these methods have been reported to give deoxygenation efficiencies of 95% or greater depending upon the amount of time the procedure is used.

Novel Methods. Several novel approaches have also been reported for oxygen removal from liquid samples. MacCrehan and May presented a chemical method for oxygen removal based on the use of a column packed with zinc particles (3). The zinc scrubber column eliminated

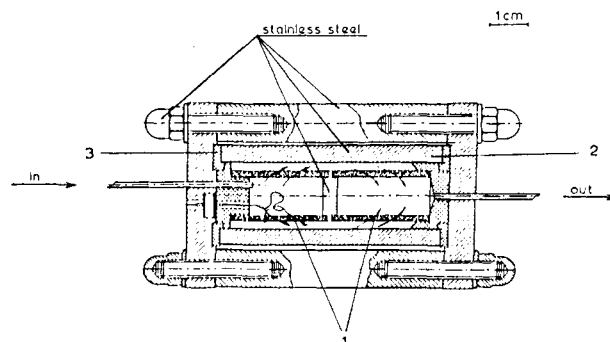


Figure 1. Electrochemical eluent scrubber used by Frei et al.: (1) porous silver electrodes; (2) steel housing, counter electrode; (3) Delrin seals. Reprinted with permission from: Hanekamp, H. B.; Voogt, W. H.; Bos, P.; Frei, R. W. *Anal. Chim. Acta* 1980, 118, 81-86. Copyright 1980 Elsevier Scientific Publishing Company.

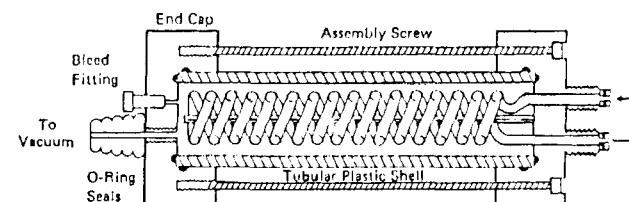
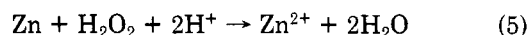
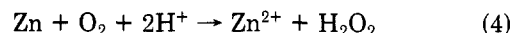


Figure 2. Tubular semipermeable membrane deoxygenator used by Reim. Reprinted with permission from ref 5. Copyright 1983 American Chemical Society.

dissolved oxygen from liquid chromatographic eluents by reduction of the oxygen to water via the two-step process shown in reactions 4 and 5. The columns were found to



be very effective in preventing oxygen interference in reductive amperometry and molecular fluorescence detection systems for high-performance liquid chromatography. Frei et al. described an electrochemical scrubber containing porous silver electrodes for use in liquid chromatography with reductive electrochemical detection (LCEC) (4). To eliminate oxygen and electrochemically active impurities, a cell with porous silver flow-through electrodes was placed in the eluent stream. The impurities were removed by applying a negative potential at the electrodes. This scrubber is shown in Figure 1. Reim reported the use of a tubular semipermeable membrane as a postcolumn deoxygenator for LCEC (5). In this approach, a tubular silicone rubber membrane was enclosed in a plastic shell as shown in Figure 2. Oxygen transport across the membrane was facilitated by evacuation of the outer shell. Reim reported this device to be 98% efficient for the removal of dissolved oxygen from 0.1 M HClO₄ electrolyte solution. Trojānek and Holub reported the use of a similar tubular silicone rubber membrane for continuous removal of oxygen from liquid samples (6). Again, oxygen diffused through a semipermeable membrane into a space with a lower partial pressure. The efficiency of oxygen removal was reported to be "quite high" and strongly dependent on the parameter of the length of flow through the degassing apparatus divided by the average flow rate of the solution (6). In membrane separation systems, deoxygenation efficiency is controlled by the solubility coefficient of oxygen in the membrane and the diffusion rate of oxygen through the membrane (the product of these terms is equal to the permeability coefficient of oxygen in the membrane) and the oxygen partial pressure difference through the membrane. Another deoxygenator based on a semipermeable membrane was reported by Rollie et al.

Tubing (Membrane Permeable to Oxygen)

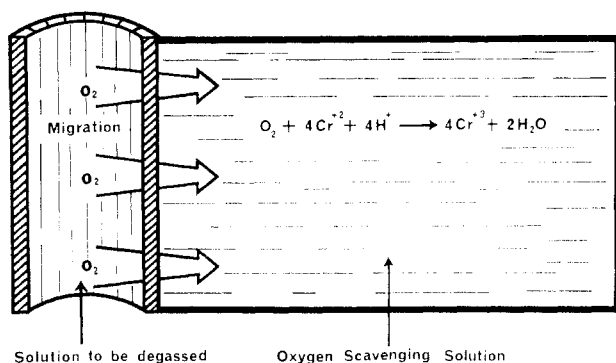
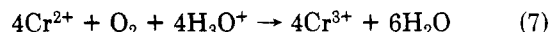
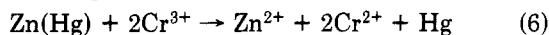


Figure 3. Cross section of solution undergoing deoxygenation by chromium(II) through an oxygen-permeable membrane. Reprinted with permission from ref 7. Copyright 1983 American Chemical Society.

(7). In this procedure, a strongly reducing chromium(II) solution, generated in the presence of amalgamated zinc, was used to create an oxygen concentration gradient through the membrane. As oxygen diffused through the membrane to reduce the pressure difference, it was reduced to water by the acidic chromium(II) solution, as shown in the sequence of reactions 6 and 7. A schematic



representation of this process is shown in Figure 3. A commercial degasser that also works on the principle of membrane separation is the ERC-3000 degasser (75). Oxygen diffusion through the tubular plastic membrane is facilitated by evacuation of the chamber in which the membrane is housed. This degasser has been used primarily in HPLC. However, the device can be used with other instruments by means of a pipe connection. Other commercially available degassers have also been described, such as built-in HPLC degassers most of which work by inert gas purging.

Applications of Sample Deoxygenation

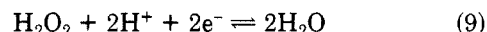
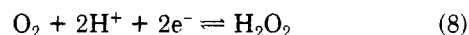
Since the presence of dissolved oxygen causes a variety of adverse effects in many analytical procedures, numerous approaches for sample and eluent deoxygenation are used. Having presented a survey of the deoxygenation techniques, some of the analytical procedures to which such methodology can be applied will now be discussed. These techniques include spectroscopy, electrochemistry, and chromatography. Although these all represent important areas in analytical chemistry, other areas of chemistry can also benefit by use of any of these deoxygenation methods.

Spectroscopy. Both fluorescence and phosphorescence analysis are limited by the presence of dissolved oxygen. Molecular oxygen quenches the excited species considerably in fluorescence analysis (3, 7, 9–28) and completely in phosphorescence analysis (33–40) unless preventative measures are taken. In fluorescence analysis, the excited singlet state is dynamically quenched by molecular oxygen. This results in a decrease in the overall fluorescence intensity because a portion of the excited singlet molecules return to the ground state via the nonradiative deexcitation (i.e., quenched) pathway (15–28). Numerous studies have been devoted to investigation of the nature of the interactions that are responsible for the nonradiative deexcitation pathway (15–28). Interested readers may consult any of several references (15–28) for a more detailed explanation of these processes.

Fluorescence quenching by oxygen is not as severe as is phosphorescence quenching because of the relatively short lifetime of the excited singlet state (approximately 1×10^{-8} s) (9–13, 39). Conversely, because of the long triplet-state lifetime (1×10^{-3} – 10 s) and the fact that excited molecules tend to return to the ground state via the pathway that most greatly minimizes the lifetime of the excited state, oxygen completely quenches phosphorescence in solution (33–40).

Owing to the potency of oxygen quenching of luminescence, sample deoxygenation is an important preparatory step in most fluorimetric and all solution phosphorimetric analysis procedures. Of the previously mentioned degassing procedures, nitrogen purging (14, 29–32) and freeze-pump-thaw cycles (86) have been most often reported for luminescence samples. The zinc-oxygen scrubber column developed by MacCrehan and May was also applied to remove oxygen in fluorescence detected HPLC analysis (3). The membrane separation method of sample deoxygenation that was developed by Rollie et al. was also applied to fluorescence analysis (7, 8). When this procedure was applied using several amounts of equilibration time, the intensity of pyrene fluorescence was enhanced by factors of 13.6–18.7 (8).

Electrochemistry. As in luminescence analysis, oxygen removal prior to reductive electrochemical analysis improves the sensitivity and precision of this procedure. A common problem in reductive electrochemical analysis is the high background current, and resulting base-line noise, caused by the reduction of electroactive impurities in the eluent (3, 45, 47, 48, 52, 66). One of the major impurities is dissolved oxygen. The presence of dissolved oxygen in electroanalytical samples can result in high background currents that interfere with analyte measurements due to the reduction of oxygen to hydrogen peroxide and water as shown in reactions 8 and 9. Therefore, polarographic



(3, 45, 47, 48, 52, 66), amperometric (64, 65), and coulometric (49) determinations can all be improved via deoxygenation prior to analysis. Of the previously surveyed techniques, nitrogen purging (41–43, 46, 47, 66), argon purging (48), and vacuum degassing (49) were reported most frequently as the methods used for oxygen removal. For example, Wang and Ariel reported a continuous deaeration system that utilized nitrogen purging through a sintered glass disk to attain intimate contact between the sample and the gas bubbles (46). The system was used for deoxygenation of sea-water samples prior to voltammetric analysis. However, the continuous deaeration chamber is applicable to other modes of analysis. The efficiency of oxygen removal with this continuous system was reported to be equivalent to nitrogen purging of a stagnant sample for 10 min. Hawkridge and Kuwana used evacuation followed by nitrogen purging in three cycles to deaerate heme protein samples prior to coulometric titration (49). Residual oxygen levels were reduced to less than 4×10^{-7} M by using this procedure. Bowden et al. also reported using evacuation/nitrogen purge cycles to prepare protein samples for anaerobic cyclic voltammetric analysis (44). Anaerobic solution conditions (i.e., less than $1 \mu\text{M}$ oxygen) were reportedly attained by using deoxygenation and a specially designed optically transparent thin-layer electrochemical cell.

Chromatography. Analogous to luminescent and electrochemical methods of analysis, high-performance liquid chromatography (HPLC) can also be plagued by

problems owing to the presence of dissolved oxygen in the mobile phase (53–61). Dissolved oxygen gives rise to such problems as damage to labile stationary phases (58) and base-line drift resulting from UV absorbance by some organic solvents, particularly in the far UV (56). However, the most common problem is that of noise and drift caused by outgassing at the detector. Air dissolved in the mobile phase at high pressures can form bubbles at the low-pressure detector end of the chromatographic system. The result is noise in the base line when the bubbles pass through the detector (56). When HPLC with fluorescence detection is the method of analysis, obviously, all of the inherent problems resulting from oxygen quenching of fluorescence are accrued in addition to most of those already noted for HPLC with conventional UV detection (14, 56). Therefore, degassing of the mobile phase prior to HPLC analysis offers several benefits including minimization of detector problems, improved pumping precision, protection of stationary phases, and more stable base lines (54, 56, 58). Inert gas purging, primarily by using helium, is the most frequently reported degassing method used for HPLC mobile phases (54, 56). However, refluxing (54, 56), evacuation (54, 56), and ultrasonification (54, 57, 61) have also been evaluated with respect to their applicability to HPLC.

Liquid chromatography with reductive electrochemical detection (LCEC), obviously, has two sets of oxygen-related problems: i.e., those previously described for reductive electrochemical analysis and most of those encountered in HPLC analysis. Consequently, solution deoxygenation is often a necessary preparative procedure. Frei et al. reported use of the electrochemical scrubber that was highlighted in the Novel Methods section to remove oxygen and other electroactive impurities prior to polarographic detection (4). The impurities were removed by applying a negative electrode potential. A 100-fold reduction of background current and a 10-fold reduction of base-line noise in comparison to nitrogen purging of the eluent were reportedly achieved (4). Although applied to electrochemical analysis, this scrubber technique can be used for other detection systems. Reim reported the use of the tubular semipermeable membrane, which was also previously described, for continuous deoxygenation of chromatographic effluents via oxygen diffusion across the membrane into an evacuated outer shell prior to reductive electrochemical detection (5). The apparatus was reported to be 98% efficient for oxygen removal from some electrochemical solutions (5). Among the other deoxygenation techniques reported for LCEC are evacuation (62–63), nitrogen purging (65–67), and argon purging (64).

Thus, four frequently used analytical methods, luminescence spectroscopy, reductive electrochemical analysis, high-performance liquid chromatography, and liquid chromatography with reductive electrochemical detection, are all hindered by problems that arise from the presence of dissolved oxygen in the sample matrix. However, each is used routinely for sensitive analytical determination following the application of one of several currently used deoxygenation procedures. These procedures vary from fairly simple to somewhat complex. Each has its own advantages and limitations with respect to implementation time, oxygen removal efficiency, and required sample handling. These are the relevant factors that have to be considered when evaluating the feasibility of a deoxygenation procedure.

Summary

We have sought to present a representative, as opposed to an exhaustive, survey of the necessity for and metho-

dology for achieving oxygen-free samples and solvents. Since oxygen-related problems are prevalent in many areas of analysis, numerous methods of deoxygenation have been developed. These methods provide varied approaches to what may initially seem to be a difficult task, i.e., elimination of oxygen from analytical solvents and samples. This methodology of sample deoxygenation has many and frequent applications because four areas in analytical chemistry alone are all touched by oxygen-induced problems. Therefore, while the conventional deoxygenation methods are certain to continue to be useful, new methods are also to be expected. These methods will be characterized by those factors that make current degassing methods useful. These factors include efficiency of oxygen removal, ease of implementation, and amount of required sample handling. The sample handling factor can be expected to become less of a consideration as solution deoxygenation, as is true for many other analytical procedures, progresses more and more from manual implementation to automated applications.

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