change resin binds Cu^{2+} and replaces it with $2H^+$. The anion-exchange resin binds NO_3^- and replaces it with OH^-. The eluate is pure water:

$$\left.\begin{array}{l} Cu^{2+} \xrightarrow{H^+ \text{ ion exchange}} 2H^+ \\ 2NO_3^- \xrightarrow{OH^- \text{ ion exchange}} 2OH^- \end{array}\right\} \longrightarrow \text{pure } H_2O$$

In many laboratory buildings, tap water is initially purified by passage through activated carbon (which adsorbs organic material) and then by *reverse osmosis*. In this process, water is forced by pressure through a membrane containing pores through which few molecules larger than H_2O can pass. Most ions cannot pass through the pores because their *hydrated radius* (see opening of Chapter 8) is larger than the pore size. Reverse osmosis removes about 95–99% of ions, organic molecules, bacteria, and particles from water.

"Water polishing" equipment used in many laboratories further purifies the water after reverse osmosis. The water is passed through activated carbon and then through several ion-exchange cartridges that convert ions to H^+ and OH^-. The resulting high-purity water has a resistivity (Chapter 15, note 28) of 180 000 ohm·m (18 Mohm·cm), with concentrations of individual ions below 1 ng/mL (1 ppb).[1]

26-2 Ion Chromatography

Ion chromatography, a high-performance version of ion-exchange chromatography, has become the method of choice for anion analysis.[2] For example, it is used in the semiconductor industry to monitor anions and cations at 0.1 ppb levels in deionized water.

Suppressed-Ion Anion and Cation Chromatography

In **suppressed-ion anion chromatography** (Figure 26-4a), a mixture of anions is separated by ion exchange and detected by electrical conductivity. The key feature of suppressed-ion chromatography is removal of unwanted electrolyte prior to conductivity measurement.

For the sake of illustration, consider a sample containing $NaNO_3$ and $CaSO_4$ injected into the *separator column*—an anion-exchange column in the carbonate form—followed by elution with KOH. NO_3^- and SO_4^{2-} equilibrate with the resin and are slowly displaced by the OH^- eluent. Na^+ and Ca^{2+} cations are not retained and simply wash through. After a period of time, KNO_3 and K_2SO_4 are eluted from the separator column, as shown in the upper graph of Figure 26-4a. These species cannot be easily detected, however, because the solvent contains a high concentration of KOH, whose high conductivity obscures that of the analyte species.

To remedy this problem, the solution next passes through a *suppressor*, in which cations are replaced by H^+. H^+ exchanges with K^+, in this example, through a cation-exchange membrane in the suppressor. H^+ diffuses from high concentration outside the membrane to low concentration inside the membrane. K^+ diffuses from high concentration inside to low concentration outside. K^+ is carried away outside the membrane, so its concentration is always low on the outside. The net result is that KOH eluent, which has high conductivity, is converted to H_2O, which has low conductivity. When analyte is present, HNO_3 or H_2SO_4 with high conductivity is produced and detected.

Suppressed-ion cation chromatography is conducted in a similar manner, but the suppressor replaces Cl^- from eluent with OH^- through an anion-exchange membrane. Figure 26-4b illustrates the separation of $NaNO_3$ and $CaSO_4$. With HCl eluent, NaCl and $CaCl_2$ emerge from the cation-exchange separator column, and NaOH and $Ca(OH)_2$ emerge from the suppressor column. HCl eluate is converted to H_2O in the suppressor. In highly automated systems, H^+ and OH^- eluents and suppressors are generated electrolytically without intervention by the operator.[3]

Figure 26-5 illustrates a student experiment to measure ions in pond water. Eluent for the anion separation was $NaHCO_3/Na_2CO_3$ buffer. The product from eluent after passing through the suppressor is H_2CO_3, which has low conductivity.

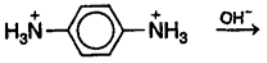
What are the ions in pristine snow? Antarctic snow provides a measure of global atmospheric chemistry because there are no local sources of pollution. One study found the following species by ion chromatography:

Ion	Concentrations observed (μg/L = ppb) Minimum	Maximum
F^-	0.10	6.20
Cl^-	25	40 100
Br^-	0.8	49.4
NO_3^-	8.6	354
SO_4^{2-}	10.6	4 020
$H_2PO_4^-$	1.8	49.0
HCO_2^-	1.1	45.7
$CH_3CO_2^-$	5.0	182
$CH_3SO_3^-$	1.1	281
NH_4^+	2.4	46.5
Na^+	15	17 050
K^+	3.1	740
Mg^{2+}	2.7	1 450
Ca^{2+}	12.6	1 010

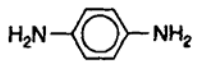
SOURCE: R. Udisti, S. Bellandi, and G. Piccardi, "Analysis of Snow from Antarctica," *Fresenius J. Anal. Chem.* **1994**, *349*, 289.

The separator column separates the analytes, and the suppressor replaces the ionic eluent with a nonionic species.

Benzene-1,4-diammonium cation is a stronger eluent that can be used instead of H^+ for suppressed-ion cation chromatography. After passing through the suppressor column, a neutral product is formed:



Benzene-1,4-diammonium ion



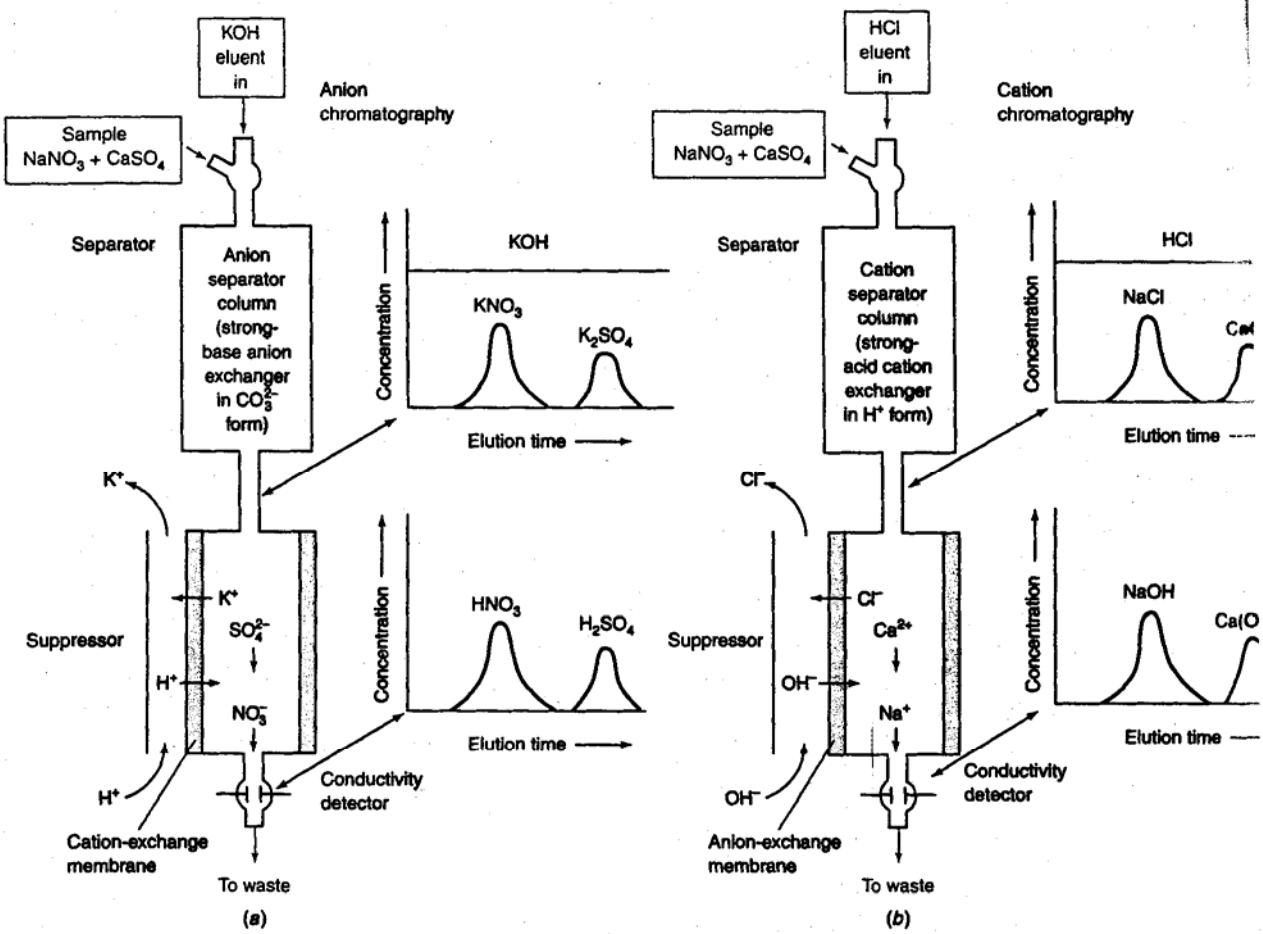


Figure 26-4 Schematic illustrations of (*a*) suppressed-ion anion chromatography and (*b*) suppressed-ion cation chromatography.

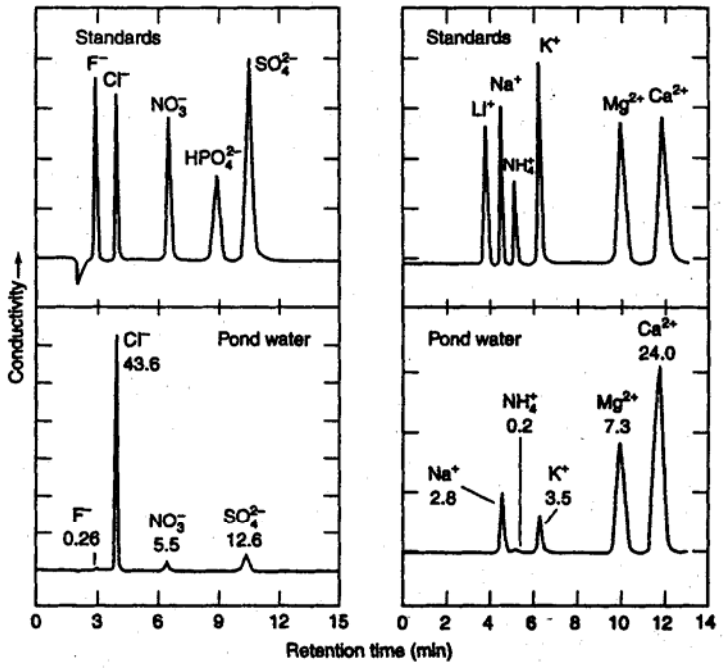
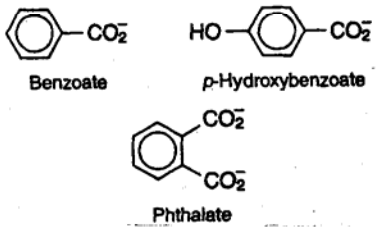


Figure 26-5 Ion chromatography of pond water. Upper chromatograms were obtained from mixtures of standards. Concentrations of ions in lower chromatograms from pond water are in units of μg/mL (ppm). Anion analysis was done with an IonPac AS14 column using 1.0 mM $NaHCO_3$/3.5 mM Na_2CO_3 eluent with ion suppression and conductivity detection. Cation analysis used an IonPac CS12A column with 11 mM H_2SO_4 eluent, ion suppression, and conductivity detection. [From K. Sinniah and K. Piers, "Ion Chromatography: Analysis of Ions in Pond Waters," *J. Chem. Ed.* **2001**, *78*, 358.]

Chromatography Without Suppression

e ion-exchange capacity of the separator column is sufficiently low and if dilute nt is used, ion suppression is unnecessary. Also, anions of weak acids, such as te, silicate, sulfide, and cyanide, cannot be determined with ion suppression use these anions are converted into very weakly conductive products (such as H_2S).

For *nonsuppressed anion chromatography*, we use a resin with an exchange capacnear 5 μequiv/g, with 10^{-4} M Na^+ or K^+ salts of benzoic, *p*-hydroxybenzoic, or halic acid as eluent. These eluents give a low background conductivity, and analyte ons are detected by a small *change* in conductivity as they emerge from the column. udicious choice of pH, an average eluent charge between 0 and −2 can be obtained, ich allows control of eluent strength. Even dilute carboxylic acids (which are slightly ized) are suitable eluents for some separations. *Nonsuppressed cation chromatogra*y is conducted with dilute HNO_3 eluent for monovalent ions and ethylenediammom salts ($^+H_2NCH_2CH_2NH_2^+$) for divalent ions.



etectors

onductivity detectors respond to all ions. In suppressed-ion chromatography, it is easy measure analyte because eluent conductivity is reduced to near 0 by suppression. uppression also allows us to use eluent concentration gradients.

In nonsuppressed anion chromatography, the conductivity of the analyte anion is igher than that of the eluent, so conductivity increases when analyte emerges from e column. Detection limits are normally in the mid-ppb to low-ppm range but can be owered by a factor of 10 by using carboxylic acid eluents instead of carboxylate salts.

Using benzoate or phthalate eluents provides for sensitive (<1 ppm) **indirect detection** of anions. In Figure 26-6, eluate has strong, constant ultraviolet absorption. As each analyte emerges, nonabsorbing analyte anion replaces an equivalent amount of absorbing eluent anion. Absorbance therefore *decreases* when analyte appears. For cation chromatography, $CuSO_4$ is a suitable ultraviolet-absorbing eluent.

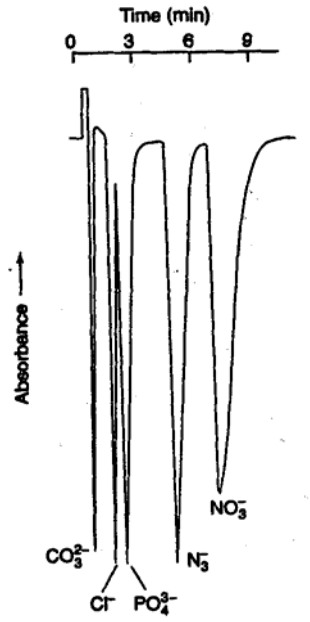


Figure 26-6 Indirect spectrophotometric detection of transparent ions. The column was eluted with 1 mM sodium phthalate plus 1 mM borate buffer, pH 10. [Reproduced from H. Small, "Indirect Photometric Chromotography," *Anal. Chem.* 1982, *54*, 462.] The principle of indirect detection is illustrated in Figure 26-27.

Ion-Pair Chromatography

Ion-pair chromatography uses a reversed-phase HPLC column instead of an ion-exchange column. To separate a mixture of cations (e.g., protonated organic bases), an anionic *surfactant* (Box 26-1) such as n-$C_8H_{17}SO_3^-$ is added to the mobile phase. The surfactant lodges in the stationary phase, effectively transforming the stationary phase into an ion exchanger (Figure 26-7). When analyte cations pass through the column,

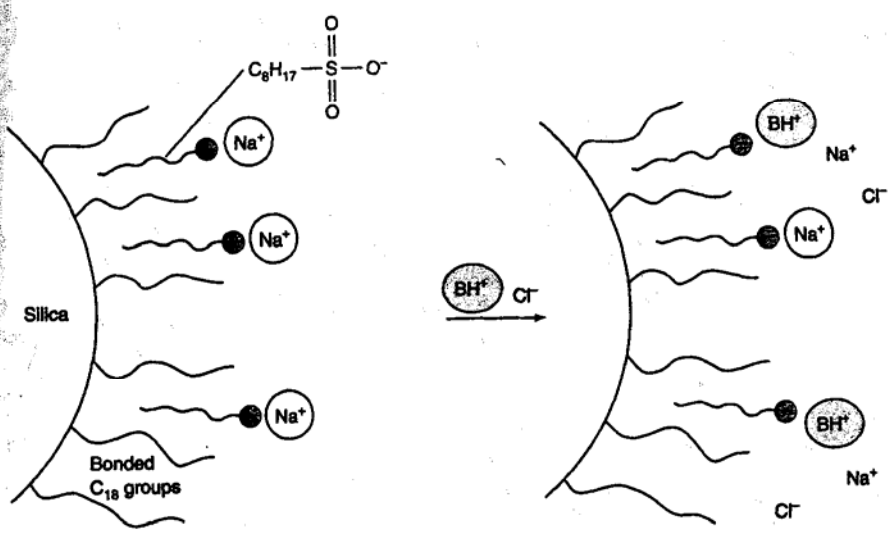
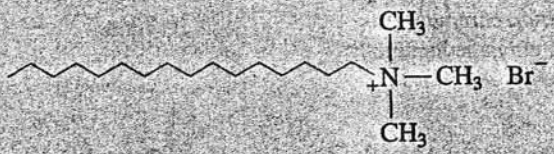


Figure 26-7 Principle of ion-pair chromatography. The surfactant sodium octanesulfonate added to the mobile phase binds to the nonpolar stationary phase. Negative sulfonate groups protruding from the stationary phase then act as ion-exchange sites for analyte cations such as protonated organic bases, BH^+.

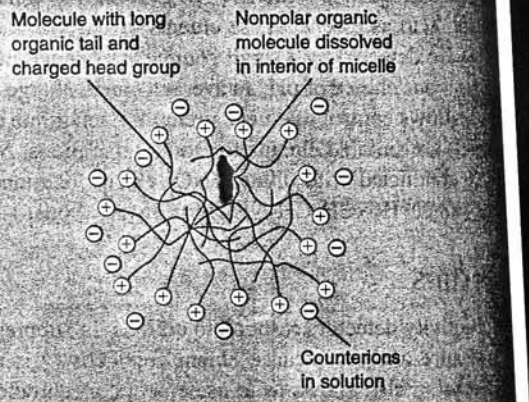
Box 26-1 Surfactants and Micelles

A **surfactant** is a molecule that accumulates at the interface between two phases and modifies the surface tension. (*Surface tension* is the energy per unit area needed to form a surface or interface.) One common class of surfactants for aqueous solution are molecules with long hydrophobic tails and ionic headgroups, such as



Cetyltrimethylammonium bromide
$C_{16}H_{33}N(CH_3)_3^+Br^-$

A **micelle** is an aggregate of surfactants. In water, the hydrophobic tails form clusters that are, in effect, little oil drops insulated from the aqueous phase by the ionic head groups. At low concentration, surfactant molecules are not associated. When their concentration exceeds the *critical micelle concentration*, spontaneous aggregation into micelles begins to occur.[4] Isolated surfactant molecules exist in equilibrium with micelles. Nonpolar organic solutes are solubilized inside micelles.



Structure of a micelle formed when ionic molecules with long, nonpolar tails aggregate in aqueous solution. The interior of the micelle resembles a nonpolar organic solvent, whereas the exterior charged groups interact strongly with water. [F. M. Menger, R. Zana, and B. Lindman, "Portraying the Structure of Micelles," *J. Chem. Ed.* **1998**, *75*, 115.]

they can associate with the stationary phase by electrostatic attraction to the surface anions.[5] The retention mechanism is a mixture of reversed-phase and ion-exchange interactions. To separate analyte anions, tetrabutylammonium salts can be added to the mobile phase as the ion-pair reagent (Figure 26-8).

Ion-pair chromatography is more complex than reversed-phase chromatography because equilibration of the surfactant with the stationary phase is slow, the separation

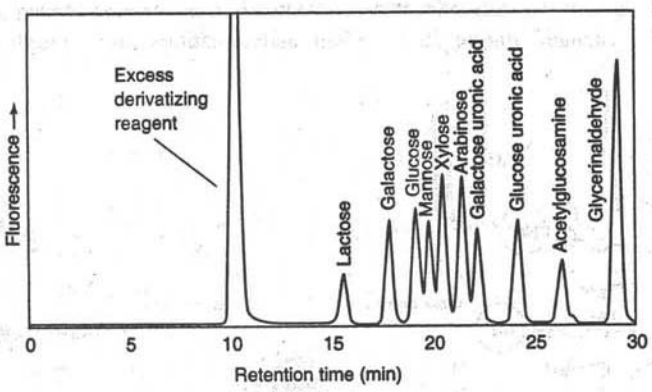


Figure 26-8 Separation of carbohydrates by ion-pair chromatography. Carbohydrates were *derivatized* by covalently attaching *p*-aminobenzoate ($H_2N—C_6H_4—CO_2^-$), which changes carbohydrates into fluorescent anions. The anions were separated on a 0.30 × 25 cm column of AQUA® C_{18}-silica, using tetrabutylammonium cation as the ion-pair reagent. Eluent was a linear 60-min gradient starting with 20 mM aqueous $(n\text{-}C_4H_9)_4N^+HSO_4^-$, pH 2.0 (solvent A) and ending with 50:50 A/methanol. The method was used to measure carbohydrates at 10–100 ng/mL levels in water leaching from landfills. [From A. Meyer, C. Raba, and K. Fischer, "Ion-Pair HPLC Determination of Sugars, Amino Sugars, and Uronic Acids," *Anal. Chem.* **2001**, *73*, 2377.]

HOI: hypoiod
IO_3^-: iodate

Because the equilibrium constant is small, $[H^+]$ must be kept low to ensure complete reaction. If $[H^+]$ is *too* small (pH $\gtrsim$ 11), triiodide disproportionates to hypoiodous acid, iodate, and iodide. Standardization is usually carried out at pH 7–8 in bicarbonate buffer.

An excellent way to prepare standard I_3^- is to add a weighed quantity of potassium iodate to a small excess of KI.[17] Then add excess strong acid (giving pH $\approx$ 1) to produce I_3^- by quantitative reverse disproportionation:

$$\underset{(KIO_3\ \text{primary standard})}{IO_3^-} + 8I^- + 6H^+ \rightleftharpoons 3I_3^- + 3H_2O \qquad \textbf{(16-18)}$$

Freshly acidified iodate plus iodide can be used to standardize thiosulfate. The I_3^- must be used immediately, or else it is oxidized by air. The only disadvantage of KIO_3 is its low molecular mass relative to the number of electrons it accepts. This property leads to a larger than desirable relative weighing error in preparing solutions.

Box 16-1 Environmental Carbon Analysis and Oxygen Demand

Drinking water and industrial waste streams are partially characterized and regulated on the basis of their carbon content and oxygen demand.[8] *Inorganic carbon* (IC) is defined as the $CO_2(g)$ liberated when water is acidified to pH < 2 with H_3PO_4 and purged with Ar or N_2. IC corresponds to CO_3^{2-} and HCO_3^- in the sample. After inorganic carbon is removed by acid, *total organic carbon* (TOC) is equated to the CO_2 produced by oxidizing organic matter in the water:

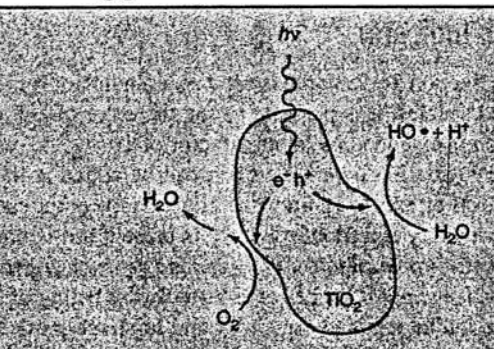
$$\text{TOC analysis:}\quad \text{Organic carbon} \xrightarrow[\text{metal catalyst}]{O_2\ /\ \sim 700^\circ C} CO_2$$

Tap water typically contains a TOC content of 50–500 ng C/mL. *Total carbon* (TC) is defined as the sum TC = TOC + IC.

Instruments using different oxidation techniques produce different values for TOC, because not all organic matter is oxidized by each technique. The current state of the art is such that TOC is really defined by the result obtained with a particular instrument.

Commercial instruments that measure TOC by thermal oxidation have detection limits of 4–50 ppb (4–50 μg C/L). A typical 20-μL water sample is analyzed in 3 min, using infrared absorption to measure CO_2. Other instruments oxidize organic matter by irradiating a suspension of solid TiO_2 catalyst (0.2 g/L) in water at pH 3.5 with ultraviolet light.[9] Light creates electron-hole pairs (Section 15-8) in the TiO_2.[10] Holes oxidize H_2O to hydroxyl radical (HO·), a powerful oxidant that converts organic carbon to CO_2, which is measured by the electrical conductivity of carbonic acid. Color Plate 10 shows an instrument in which $K_2S_2O_8$ in acid is exposed to ultraviolet radiation to generate sulfate radical (SO_4^-), which oxidizes organic matter to CO_2.

Total oxygen demand (TOD) tells us how much O_2 is required for complete combustion of pollutants in a waste stream. A volume of N_2 containing a known quantity of O_2 is mixed with the sample and complete combustion is carried out. The remaining O_2 is measured by a potentiometric sensor (Box 17-1). Different species in the waste stream consume different amounts of O_2. For example, urea consumes five times as much O_2 as formic acid does. Species such as NH_3 and H_2S also contribute to TOD.



Ultraviolet radiation absorbed by TiO_2 creates an electron-hole pair. The hole oxidizes H_2O to the powerful oxidant HO·. The electron reduces dissolved O_2 to H_2O by a chain of reactions. TiO_2 is a catalyst and O_2 is consumed in the net reaction: organic C + $O_2 \rightarrow CO_2$.

Pollutants can be oxidized by refluxing with dichromate ($Cr_2O_7^{2-}$). *Chemical oxygen demand* (COD) is defined as the O_2 that is chemically equivalent to the $Cr_2O_7^{2-}$ consumed in this process. Each $Cr_2O_7^{2-}$ consumes 6e^- (to make 2Cr^{3+}) and each O_2 consumes 4e^- (to make H_2O). Therefore, 1 mol of $Cr_2O_7^{2-}$ is chemically equivalent to 1.5 mol of O_2 for this computation. COD analysis is carried out by refluxing polluted water for 2 h with excess standard $Cr_2O_7^{2-}$ in H_2SO_4 solution containing Ag^+ catalyst. Unreacted $Cr_2O_7^{2-}$ is then measured by titration with standard Fe^{2+} or by spectrophotometry. Permits for industrial operations may include COD limits for the waste streams. The quantity "oxidizability," which is used in Europe, is analogous to COD. Oxidizability

Sodium Thiosulfate

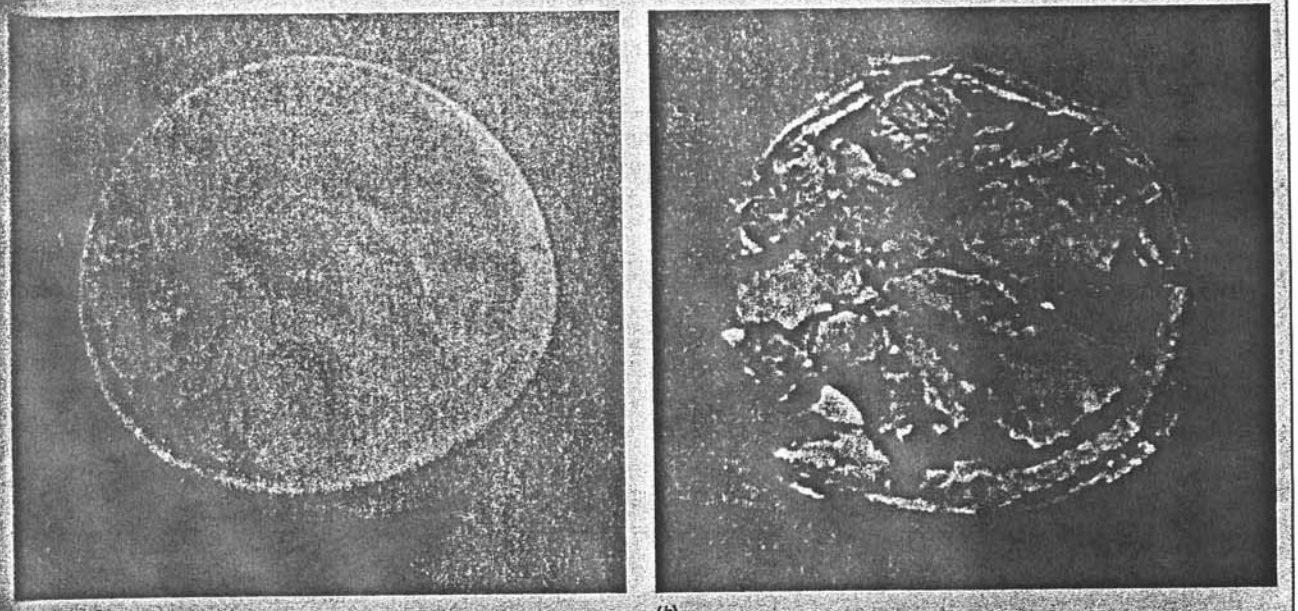
thiosulfate is the almost universal titrant for triiodide. In neutral or acidic solu- iodide oxidizes thiosulfate to tetrathionate:

$$I_3^- + 2S_2O_3^{2-} \rightleftharpoons 3I^- + O{=}S(O^-){-}S{-}S{-}S(O^-){=}O \qquad (16\text{-}19)$$

Thiosulfate → Tetrathionate

ic solution, I_3^- disproportionates to I^- and HOI, which can oxidize $S_2O_3^{2-}$ to SO_4^{2-}. tion 16-19 needs to be carried out below pH 9. The common form of thiosulfate, $_2O_3 \cdot 5H_2O$, is not pure enough to be a primary standard. Instead, thiosulfate is usually

Anhydrous, primary standard $Na_2S_2O_3$ can be prepared from the pentahydrate.[18]



(a) TiO_2-blended PVC before irradiation

(b) After irradiation for 20 days

Here is a "green" idea: TiO_2 can be blended into polyvinyl chloride (PVC) plastic so that the plastic degrades in sunlight.[11] Ordinary PVC lasts many years in municipal landfills after it is discarded. TiO_2-blended PVC would decompose in a short time. [Courtesy H. Hidaka and S. Horikoshi, Meisei University, Tokyo.]

is measured by refluxing with permanganate in acid solution at 100°C for 10 min. Each MnO_4^- consumes five electrons and is chemically equivalent to 1.25 mol of O_2.

Biochemical oxygen demand (BOD) is defined as the O_2 required for biochemical degradation of organic materials by microorganisms. The procedure calls for incubating a sealed container of wastewater with no extra air space for 5 days at 20°C in the dark while microbes metabolize organic compounds in the waste. The O_2 dissolved in the solution is measured before and after the incubation. The difference is BOD.[12] BOD also measures species such as HS^- and Fe^{2+} that may be in the water. Inhibitors are added to prevent oxidation of nitrogen species such as NH_3. There is great interest in developing a rapid analysis to provide information equivalent to BOD. For example, if ferricyanide ($Fe(CN)_6^{3-}$) replaces O_2 as the electron sink for bacterial degradation of organic matter, the analysis time could be reduced to 1 h.[13]

standardized by reaction with a fresh solution of I_3^- prepared from KIO_3 pl... solution of I_3^- standardized with As_4O_6.

A stable solution of $Na_2S_2O_3$ can be prepared by dissolving the reagen... quality, freshly boiled distilled water. Dissolved CO_2 makes the solution acidi... motes disproportionation of $S_2O_3^{2-}$:

$$S_2O_3^{2-} + H^+ \rightleftharpoons \underset{\text{Bisulfite}}{HSO_3^-} + \underset{\text{Sulfur}}{S(s)}$$

and metal ions catalyze atmospheric oxidation of thiosulfate:

$$2Cu^{2+} + 2S_2O_3^{2-} \rightarrow 2Cu^+ + S_4O_6^{2-}$$

$$2Cu^+ + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Cu^{2+} + H_2O$$

Thiosulfate solutions should be stored in the dark. Addition of 0.1 g of sodium ... ate per liter maintains the pH in an optimum range for stability of the solution... drops of chloroform should also be added to each bottle of thiosulfate solution...

Table 16-4 Titrations with standard triiodide (iodimetric titrations)

Species analyzed	Oxidation reaction	Notes
As^{3+}	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$	Titrate directly in $NaHCO_3$ solut... with I_3^-.
Sn^{2+}	$SnCl_4^{2-} + 2Cl^- \rightleftharpoons SnCl_6^{2-} + 2e^-$	Sn(IV) is reduced to Sn(II) with ... granular Pb or Ni in 1 M HCl ... titrated in the absence of oxyg...
N_2H_4	$N_2H_4 \rightleftharpoons N_2 + 4H^+ + 4e^-$	Titrate in $NaHCO_3$ solution.
SO_2	$SO_2 + H_2O \rightleftharpoons H_2SO_3$ $H_2SO_3 + H_2O \rightleftharpoons SO_4^{2-} + 4H^+ + 2e^-$	Add SO_2 (or H_2SO_3 or HSO_3^- or ... to excess standard I_3^- in dilute ... and back-titrate unreacted I_3^- w... standard thiosulfate.
H_2S	$H_2S \rightleftharpoons S(s) + 2H^+ + 2e^-$	Add H_2S to excess I_3^- in 1 M HCl ... back-titrate with thiosulfate.
Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}	$M^{2+} + H_2S \rightarrow MS(s) + 2H^+$ $MS(s) \rightleftharpoons M^{2+} + S + 2e^-$	Precipitate and wash metal sulfide... Dissolve in 3 M HCl with excess ... standard I_3^- and back-titrate with ... thiosulfate.
Cysteine, glutathione, thioglycolic acid, mercaptoethanol	$2RSH \rightleftharpoons RSSR + 2H^+ + 2e^-$	Titrate the sulfhydryl compound at ... 4–5 with I_3^-.
HCN	$I_2 + HCN \rightleftharpoons ICN + I^- + H^+$	Titrate in carbonate-bicarbonate buf... using *p*-xylene as an extraction ... indicator.
$H_2C{=}O$	$H_2CO + 3OH^- \rightleftharpoons HCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the ... unknown. After 5 min, add HCl a... back-titrate with thiosulfate.
Glucose (and other reducing sugars)	$RCH(=O) + 3OH^- \rightleftharpoons RCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the ... sample. After 5 min, add HCl and ... back-titrate with thiosulfate.
Ascorbic acid (vitamin C)	Ascorbate + $H_2O \rightleftharpoons$ dehydroascorbate + $2H^+ + 2e^-$	Titrate directly with I_3^-.
H_3PO_3	$H_3PO_3 + H_2O \rightleftharpoons H_3PO_4 + 2H^+ + 2e^-$	Titrate in $NaHCO_3$ solution.

SECTION 1 - INTRODUCTION TO SELF-REGENERATING SUPPRESSION FOR ANION ANALYSIS

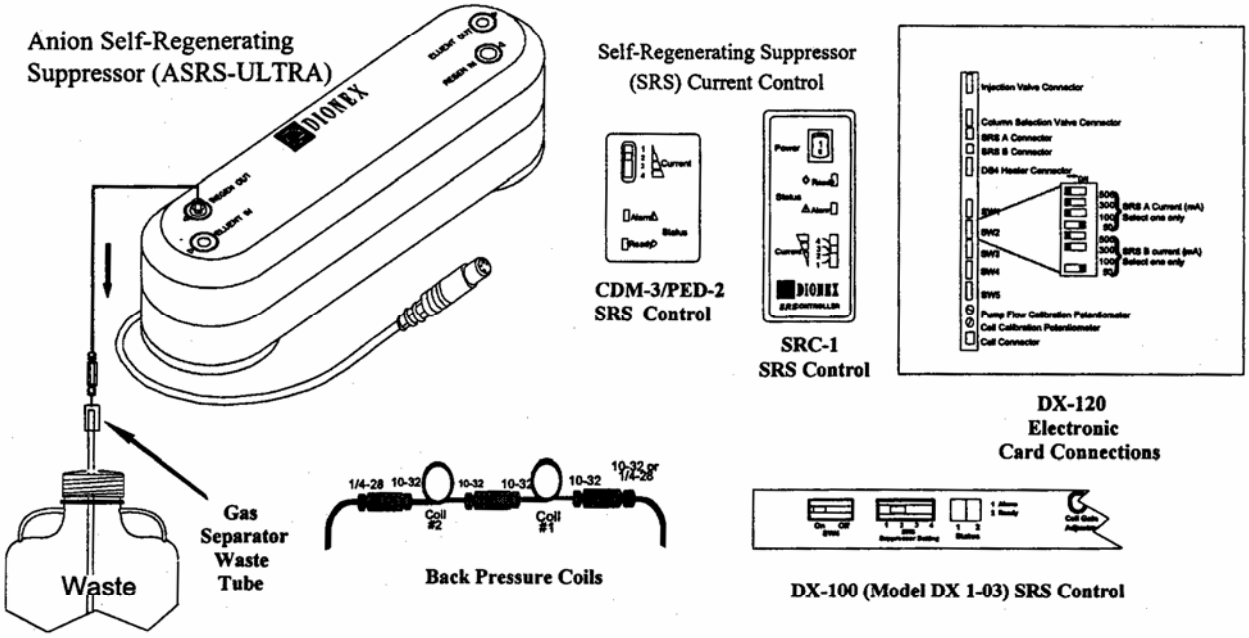


Figure 1
The Self-Regenerating Suppression System

1.1 SELF-REGENERATING SUPPRESSION SYSTEM

The Anion Self-Regenerating Suppression System consists of an Anion Self-Regenerating Suppressor (ASRS-ULTRA), the SRS® Control[1], the back pressure coils, and the Gas Separator Waste Tube. It provides a high performance, highly reliable, low maintenance AutoSuppression® system for Ion Chromatography.

The ASRS-ULTRA provides high capacity suppression while adding a minimum of dead volume to the analytical system. The ability of the ASRS-ULTRA to provide continuous suppression of traditional eluents, and more concentrated eluents up to 0.15 M NaOH, significantly expands the capabilities and simplifies the operation of anion exchange Ion Chromatography.

The ASRS-ULTRA is available in both 4-mm and 2-mm formats for use with 4-mm or 2-mm Ion Chromatography columns and systems. The 2-mm ASRS-ULTRA is specially designed with reduced internal volume to ensure optimum performance with 2-mm columns and systems. The equivalent suppression capacity of the 2-mm version of the ASRS-ULTRA, however, is greater than the suppression capacity achieved with the 4-mm version of the ASRS-ULTRA used on 4-mm Ion Chromatography systems due to the reduced eluent flow rates used on 2-mm Ion Chromatography systems but a proportionally greater surface area.

1. Integrated in the CD20 detector, the ED40 detector, the CDM-3 detector, the PED-2 detector, the DX-120, the DX-100 model 1-03 and the SRC-1 controller

Always remember that assistance is available for any problem that may be encountered during the shipment or operation of DIONEX instrumentation and columns through the DIONEX North America Technical Call Center at 1-800-DIONEX-0 (1-800-346-6390) or through any of the DIONEX Offices listed in, "DIONEX Worldwide Offices."

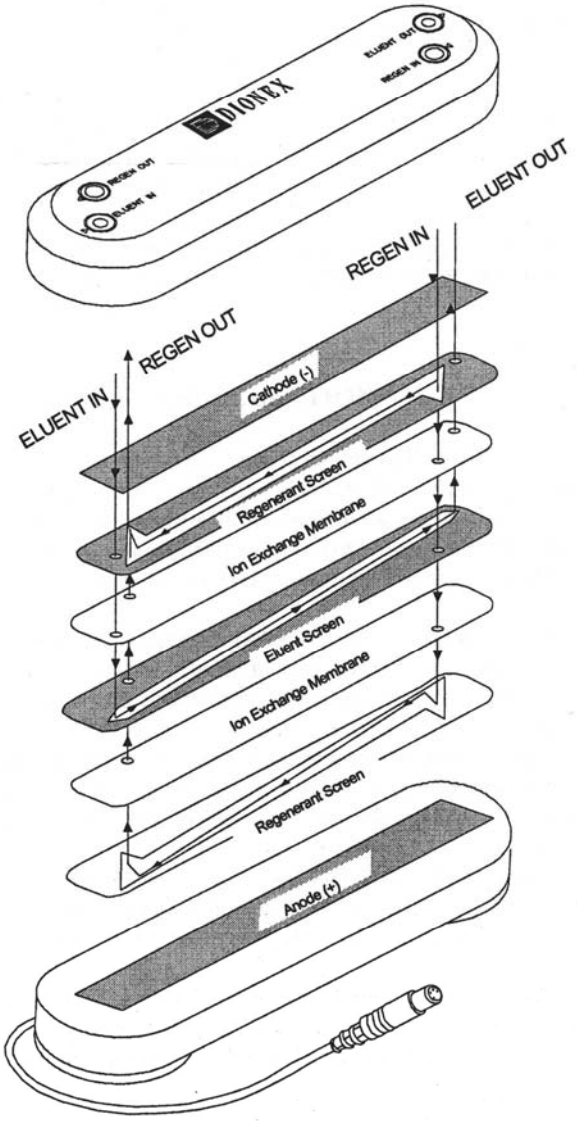


Figure 2
Electrode, Membrane and Screen Configuration in the Anion Self-Regenerating Suppressor (ASRS-ULTRA)

The ASRS-ULTRA includes two regenerant compartments and one eluent compartment separated by ion exchange membranes. Regenerant flow channels and an eluent flow channel are defined by the membrane. The eluent flow is in a direction that is countercurrent to the regenerant flow.

Electrodes are placed along the length of the regenerant channels. When an electrical potential is applied across the electrodes, water from the regenerant channels is electrolyzed, supplying regenerant hydronium ions (H_3O^+) for the neutralization reaction. The membrane allows these hydronium ions to pass into the eluent chamber resulting in the conversion of the electrolyte of the eluent to a weakly ionized form. Eluent cations are simultaneously passed into the regenerant chamber to maintain charge balance.

1.2 OVERVIEW OF SUPPRESSION MODES

There are four basic modes of suppression performed with the Anion Self-Regenerating Suppressor (ASRS-ULTRA):

- AutoSuppression Recycle Mode
- AutoSuppression External Water Mode
- Chemical Suppression Mode
- MPIC Suppression Mode

The following sections explain how each mode works and help to determine which mode or chemical regenerant to use for an application. Once the mode of operation is determined, more detailed plumbing configuration and operating instructions can be found in Section 3, "Operation."

1.3 MODE OF OPERATION SELECTION

The ASRS-ULTRA mode of operation depends mainly of your eluent composition and your analysis sensitivity requirements. Eluents containing organic solvents are not compatible with the **AutoSuppression Recycle Mode**. The **AutoSuppression External Water Mode** or the **Chemical Suppression Mode** should be used instead. The **AutoSuppression External Water Mode** also reduces detector noise levels beyond those available with the **AutoSuppression Recycle Mode**. The **MPIC Suppression Mode** is specifically designed for applications where ion pair reagents and solvents are present in the eluent.

The Anion Self-Regenerating Suppressor (ASRS-ULTRA) uses water as the regenerant to achieve eluent suppression. There are two modes of electrolytic operation. The most common mode of operation is the **AutoSuppression Recycle Mode**. In this mode of operation, eluent flows from the eluent outlet of the suppressor into the conductivity cell and is then recycled through the ASRS-ULTRA regenerant chambers. This eliminates the need for an external source of water but restricts the regenerant flow rate to the eluent flow rate. The **AutoSuppression External Water Mode** incorporates an external source of deionized water flowing through the regenerant chambers. This requires the installation of pressurized bottle system to provide an external source of water. With this configuration the regenerant flow rate is not restricted to the eluent flow rate.

The **Chemical Suppression Mode** is a nonelectrolytic mode of operation and therefore requires no current supply. This mode of operation requires the installation of equipment (either the AutoRegen Accessory equipped with an Anion AutoRegen Regenerant Cartridge or a pressurized delivery bottle system) to deliver sulfuric acid through the ASRS-ULTRA regenerant chambers.

The **MPIC Suppression Mode** is a combination of the **AutoSuppression External Water Mode** augmented with a chemical regenerant such as sulfuric acid. When the ASRS-ULTRA is operating in this mode, it uses an applied current and a constant source of dilute sulfuric acid solution from a pressurized bottle delivery system.

Table 1

Eluent Composition and Suppression Mode Compatibility				
Eluent Composition	**Auto Suppression Recycle**	**Auto Suppression External Water**	**Chemical Suppression**	**MPIC Suppression**
Aqueous Eluents	**Yes**	**Yes**	**Yes**	**N/A**
Eluents Containing Organic Solvents	**No**	**Yes**	**Yes**	**No**
Eluents Containing Ion Pair Reagents with/without Solvents	**No**	**No**	**No**	**Yes**

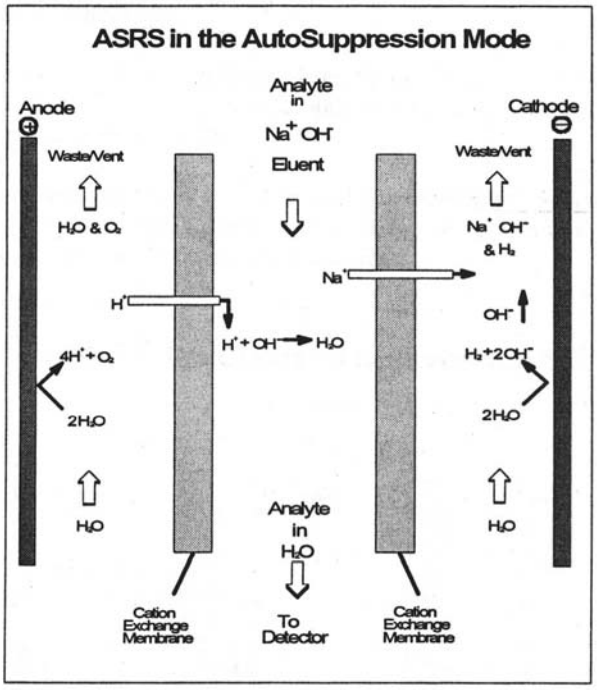


Figure 3
AutoSuppression with the Anion Self-Regenerating Suppressor (ASRS-ULTRA)

The water regenerant undergoes electrolysis to form hydrogen gas and hydroxide ions in the cathode chamber while oxygen gas and hydronium ions are formed in the anode chamber. Cation exchange membranes allow hydronium ions to move from the anode chamber into the eluent chamber to neutralize hydroxide. Sodium ions in the eluent, attracted by the electrical potential applied to the cathode, move across the membrane into the cathode chamber to maintain electronic neutrality with the hydroxide ions at the electrode. When using an eluent generator, the eluent will be potassium hydroxide instead of sodium hydroxide.

1.3.1 THE AUTOSUPPRESSION RECYCLE MODE

The **AutoSuppression Recycle Mode** uses the neutralized conductivity cell effluent as the source of water for the regenerant chamber water. This is the preferable method of operation for the ASRS-ULTRA. The advantage of this mode of operation is its simplicity and ease of use. It reliably provides AutoSuppression for most suppressed conductivity applications using solvent-free eluents. As the eluent passes through the ASRS-ULTRA, it is neutralized to its weakly ionized form. After passing through the conductivity cell, the effluent is redirected to the regenerant inlet on the ASRS-ULTRA, thus supplying it with a source of water containing minute amounts of diluted analyte. See Figure 10, "The AutoSuppression Recycle Mode Plumbing Diagram." The amount of water flowing through the regenerant chambers is therefore limited to the eluent flow rate. Because of this limitation, the **AutoSuppression Recycle Mode** of operation cannot be used with eluents containing organic solvents. See Section 3.3.3, "AutoSuppression Recycle Mode," for complete operation instructions.

1.3.2 THE AUTOSUPPRESSION EXTERNAL WATER MODE

The **AutoSuppression External Water Mode** is used for any applications requiring organic solvents in the eluent, or where reduced detector noise levels beyond those available in the recycle mode are required. This mode uses a constant source of deionized water from a pressurized bottle or other source of deionized water that delivers at least 5 to 10 mL/min. The amount of water flowing through the regenerant chambers is therefore independent of the eluent flow rate. **The AutoSuppression External Water Mode** eliminates the potential for buildup of contaminating ions resulting from the oxidation of solvents. It also reliably provides AutoSuppression for high sensitivity analysis, maximizing signal-to-noise ratios for suppressed conductivity applications. If it is determined that the system must be plumbed for applications requiring **AutoSuppression External Water Mode** remember that any analysis performed using the **AutoSuppression Recycle Mode** can also be performed using the **AutoSuppression External Water Mode.** See Section 3.4.3, "AutoSuppression External Water Mode," for complete operation instructions.

1.3.3 THE CHEMICAL SUPPRESSION MODE

The ASRS-ULTRA can also be used in the **Chemical Suppression Mode.** The chemical suppression mode should be used for applications using 40% (V/V) or more solvent. The Chemical Suppression Mode uses sulfuric (H_2SO_4) acid as a chemical regenerant instead of using an applied current and deionized water.

In this mode, the ASRS-ULTRA is operated exactly like an Anion MicroMembrane™ Suppressor (AMMS-II). Sulfuric acid is supplied to the regenerant chambers from a DIONEX AutoRegen® Accessory or a pressurized bottle delivery system. See Section 3.5.3, "Chemical Suppression Mode," for complete operation instructions.

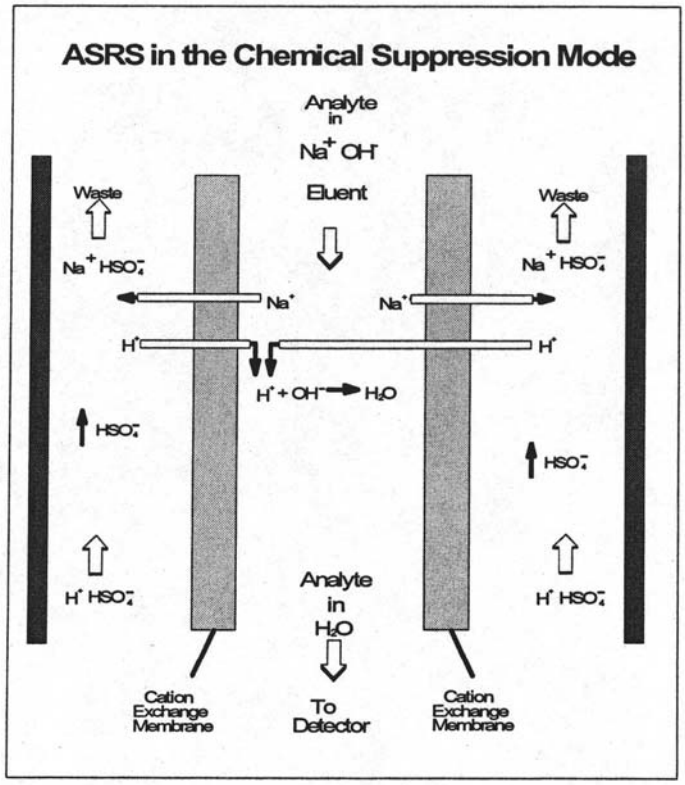


Figure 4
Chemical Suppression with the Anion Self-Regenerating Suppressor (ASRS-ULTRA)

Chemical Suppression with the ASRS is a neutralization reaction and selective desalting process carried out across the cation exchange membranes. In this mode no electrical potential is applied across the electrodes. Hydronium ions in the chemical regenerant cross the membranes and combine with the basic eluent anions, in this case hydroxide, to form water. At the same time, eluent cations cross the membranes into the regenerant stream replacing the hydronium ions.

1.3.4 THE MPIC SUPPRESSION MODE

The ASRS-ULTRA is used for eluent suppression of MPIC (ion-pairing) eluents by using the **MPIC Suppression Mode**. The **MPIC Suppression Mode** is a combination of the **AutoSuppression External Water Mode** augmented with a chemical regenerant such as sulfuric acid (H_2SO_4). The **MPIC Suppression Mode** uses an applied current and a constant source of dilute sulfuric acid solution from a pressurized bottle delivery system. This mode must be used for Mobile Phase Ion Chromatography (MPIC) applications requiring an ion pair reagent and organic solvents in the eluent. The **MPIC Suppression Mode** reliably provides suppression of typical eluents for MPIC applications using suppressed conductivity detection. The ion pair reagents, such as tetrabutylammonium hydroxide (TBAOH), are used in concentrations ranging typically from 1.0 to 5.0 mM. See Section 3.6.3, "MPIC Suppression Mode," for complete operation instructions.