

Advances in Chemical Suppression



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HISTORY OF CHEMICAL SUPPRESSION

Leading the Way in Chemical Suppression

In this brochure, Dionex invites you to learn more about suppression technology and advances in ion analysis. Dionex introduced packed-bed chemical suppression in 1975, and modern ion chromatography was born. Chemical suppression was revolutionary because it reduced background conductivity, enhancing ion detection. With packed-bed chemical suppression, chemists achieved sensitivity and selectivity from low parts-per-billion ($\mu\text{g/L}$) to parts-per-million (mg/L) levels.

Dionex continued to lead in suppression technology, introducing hollow fiber suppressors in 1981. These suppressors allowed continuous, rather than off-line regeneration used in packed-bed suppression. Dionex introduced the MicroMembrane™ suppressor (MMS) in 1985, delivering greater dynamic capacity and allowing the use of gradient elution. Dionex introduced Self-Regenerating Suppressors® (SRS®) with AutoSuppression® in 1992. These suppressors used electrolysis as the source of regenerant ions, eliminating the need to make and handle corrosive regenerant solutions.

In 2003, Dionex took suppressor technology a step further with SRS ULTRA II Suppressors. The SRS ULTRA II provided ultralow noise, low and stable backgrounds, superior dynamic capacity, and broad dynamic range. Today, the SRS 300 represents the state-of-the-art in suppressor technology. New hardware enhancements improve its backpressure tolerance threefold over previous suppressors. These improvements have also been applied to MMS products.

Packed-Bed Chemical Suppressors

A packed-bed suppressor uses a column body packed with a very high capacity ion-exchange resin. The resin is a cation exchange resin in the acid form for anion suppressors or anion exchange resin in the hydroxide form for cation suppressors. Packed-bed suppressors have finite capacity and must be taken off-line and regenerated regularly. Often they also have a very large internal volume, comparable to the separator column itself, resulting in band dispersion.

The Dionex packed-bed chemical suppressors (SC-1 and SC-2) were designed to be operated with weak eluents to maximize the time between regeneration steps. The SC-1 and SC-2 were discontinued in 1997.

The Metrohm MSM and MSM II suppressors are based on the packed-bed chemical suppression technology and are still in use to this day. In order to minimize band dispersion the MSM and MSM II have relatively low capacity, but solve this by using three suppressors which are rotated in a revolver-like device between injections. While the first one is in use, the second is being regenerated, and the third is being rinsed.

Hollow Fiber Suppressors

A hollow fiber suppressor uses a capillary (hollow fiber) that is packed with glass beads and wound onto a spool that is placed into a chamber filled with regenerant solution. The capillary is made from an ion-exchange material that allows ions to migrate into and out-of the capillary. For anion hollow fiber suppressors the capillary wall is a cation-exchange material in the acid form. For cation hollow fiber suppressors the capillary wall is an anion-exchange material in the hydroxide form. Regenerant solution is continually pumped through the regenerant chamber to keep it from becoming exhausted, while eluent is passed through the capillary.

The Dionex hollow fiber suppressor was the first continuously regenerated suppressor ever commercialized. The suppressor never needed to be taken off-line and regenerated, allowing continuous operation of the system even with moderate strength eluents. However, key disadvantages of the hollow fiber suppressor were that it easily ruptured and often the regenerant flow became restricted if the fiber swelled, resulting in excess noise.

The SeQuant SAMS™ was introduced in Sweden in 1987 and uses the same principles for suppression as the original Dionex hollow fiber suppressors.



TECHNOLOGY

MicroMembrane Suppressor

A MMS uses a pair of membranes separating a central eluent chamber from regenerant chambers on either side. The chambers are filled with functionalized ionically charged screens. In an anion MMS the membrane itself as well as screens are cation exchangers in the acid form. In a cation MMS the charge is reversed.

The Dionex MMS had substantially increased capacity compared to the hollow fiber suppressor, allowing continuous operation with moderate to strong eluents. The MMS was also more robust.

AutoRegen® for MMS

Introduced in 1987, the AutoRegen module allows continuous operation of an MMS for up to 2000 hours without the need to refill the regenerant solution, depending on the strength of the eluent being suppressed. The AutoRegen accessory is comprised of a pump, a regenerant reservoir and an AutoRegen cartridge. The pump is used to recirculate regenerant from the reservoir through the AutoRegen cartridge to the MMS and back to the

reservoir. In an AMMS for example, sulfuric acid regenerant is converted to sodium sulfate during the suppression process. The AutoRegen anion cartridge contains a high capacity cation-exchange resin in the acid form; thus sodium sulfate is converted back to sulfuric acid before re-entering the AMMS.

The SeQuant CARS uses the same principle as the Dionex AutoRegen accessory to allow continuous regeneration of a SAMS for months of unattended operation.

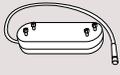
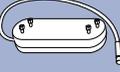
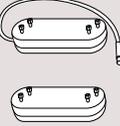
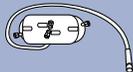
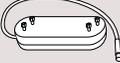
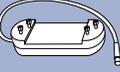
In 1999 Dionex introduced a new mode of operation for the MMS: Displacement Chemical Regeneration or DCR. In DCR mode, the effluent from the detector is used to push regenerant through the MMS regen chambers, eliminating the need for pressurized bottles or external pumps, ensuring a continuous, pulse-free flow of regenerant. The DCR mode of operation has become the recommended alternative to AutoRegen.

Self-Regenerating Suppressor

A Self-Regenerating Suppressor (SRS) has a very similar construction to a MMS, but electrodes are added to the regenerant chambers. By connecting a power supply to the electrodes and passing current through the suppressor, regenerant ions are generated inside the suppressor from water, negating the need to provide a chemical regenerant; this is known as AutoSuppression. To provide water for the electrolysis reaction, a constant flow of water is passed through the regenerant chambers.

The SRS has the highest capacity of any constantly regenerated suppressor, allowing full suppression of gradient eluents. Furthermore, by using the detector waste as regenerant, a constant flow of water is provided without the need for any secondary pumping system. This suppressor set a new standard for ease-of-use.



Year	Product		
1975 to 1997	Packed-Bed Chemical Suppressors (SC-1 and SC-2)		In 1975 Dionex changed the face of Ion Analysis forever – packed bed chemical suppression was introduced to chemists worldwide. Chemical suppression was revolutionary because it reduced background conductivity and simultaneously enhanced the detection of ions; however, the suppressor needed to be periodically taken off-line to be regenerated.
1981 to 1989	Hollow Fiber Suppressor (FS1 and FS2)		Improving on the limited capacity of the packed-bed chemical suppressors, Dionex introduced hollow fiber suppressors in 1981 which allowed continuous regeneration, eliminating the need for off-line regeneration. In 1984 a second generation hollow fiber Suppressor was introduced; this was little more than a cosmetic improvement.
1985 to 1994	MicroMembrane Suppressor (MMS™)		A few years later in 1985 the MicroMembrane suppressor was introduced. These suppressors possessed much greater dynamic capacity, increasing the flexibility of IC by allowing the use of gradient elution. The MMS was replaced by the MMS II in 1994.
1991	MMS (2-mm)		The MMS (2-mm) was the first commercially available suppressor designed for flow-rates typically found in systems using 2-mm i.d. columns. The MMS (2-mm) suppressor differed from the standard MMS (4-mm) in that the internal volume was reduced by halving the path length; thus the packaging was also smaller.
1992 to 1997	Self-Regenerating Suppressor (SRS I) and MMS II		Based on the successful design of the MMS suppressors, Self-Regenerating Suppressors (SRS) with AutoSuppression® were introduced in 1992. These suppressors used electrolysis as the source of regenerant ions for suppression, which eliminated the need to make and handle corrosive regenerant solutions altogether. The SRS-I was superseded in 1997. The MMS II was a significant improvement in the MMS design. Improved membranes led to lower backgrounds and higher efficiencies. The MMS II was replaced by the MMS III in 1998.
1997 to 1998	SRS II		The SRS II had a very similar construction to the original SRS I, but improvements were made to the screen designs in the cation version to increase solvent compatibility and overall efficiency. The SRS II was replaced by the SRS ULTRA in 1998.
1998 to 2003	SRS ULTRA and MMS III		The SRS ULTRA implemented an optimized eluent channel to reduce spiking and improve efficiencies. A new gasket design led to improved backpressure tolerance. In the cation version new screens were employed to improve current efficiency and thus decrease noise. The SRS ULTRA was replaced by the SRS ULTRA II in 2003. The MMS III was the first MMS to use the same packaging and materials as the SRS. The 2-mm version used the same channels as the SRS, improving efficiency. Other optimizations led to higher capacity and faster start-up times. The MMS III was replaced by the MMS 300 in 2007.
2001	Atlas®		In 2001 Dionex introduced a new concept in suppression technology with the Atlas Electrolytic Suppressor. The patented design of the Atlas resulted in much faster daily start-up times and lower noise. The Atlas has a significantly reduced capacity compared to MMS and SRS suppressors; however, it is still ideal for many applications.
2003 to 2007	SRS ULTRA II		The SRS ULTRA II implemented a new solvent cleaned gasket design that further reduced noise, improved efficiencies, and decreased start-up times. The cation version also implemented a new regenerant channel design that further improved performance. The SRS ULTRA II was replaced by the SRS 300 in 2007.
2007	SRS 300 and MMS 300		With the SRS ULTRA II cleaned gaskets, the SRS 300 implements a new hardware design that improves leak tolerance and increases efficiency. The MMS 300 also uses new regenerant screens that enhance dynamic capacity and increase solvent and matrix compatibility.



Atlas Suppressor

An Atlas suppressor uses a small column body packed with a series of monolithic ion exchange disks through which the eluent is passed. The ends of the column body are separated from regenerant chambers by ion exchange membranes. The regenerant chambers contain electrodes that are used to generate the regenerant ions from water. When current is applied to the electrodes, an electric field pushes the regenerant ions lengthwise through the column body counter-current to the eluent flow.

The Atlas suppressor has relatively low capacity compared to an MMS or SRS suppressor, but operates with noise levels similar to an MMS and ease-of-use similar to an SRS. Despite its low capacity, the Atlas is very well suited to a wide range of applications, particularly isocratic carbonate and methanesulfonic acid eluents.

Suppressor Availability

As Dionex advances IC technology over the years, some suppressors are discontinued to ensure that customers performing ion analysis use the best available technology. The hollow fiber suppressor was discontinued in 1989, and the packed-bed suppressor was discontinued in 1997. The AutoRegen accessory was discontinued in 2005, although AutoRegen cartridges are still available. Today, the SRS 300, MMS 300, and Atlas suppressors are the industry standard.

Leading the Way

Dionex has been at the forefront of every innovation in suppressor technology. These advances have made IC easier and more reliable, allowing chemists to consistently achieve better results. It is not surprising that IC users look to Dionex for suppressor innovations, and those advances are ongoing. Dionex's pursuit of optimal suppression has yielded the SRS 300 and MMS 300. The innovation of suppression technology will not stop there.



Dionex's goal is to provide you with solutions to your chromatographic challenges rather than just selling you an instrument. We offer more than a product; we offer a complete solution with an open future, and a partner committed to your success.



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