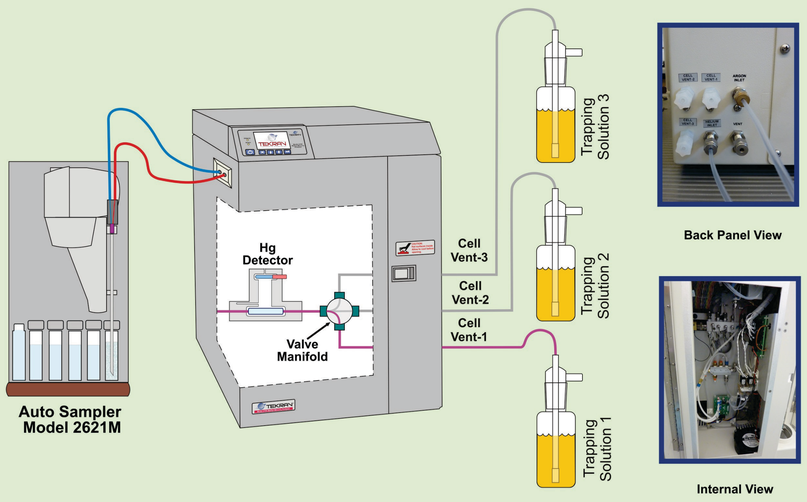
Methyl Mercury: Specialized Analytical Applications

Diana Babi*, Lucas Hawkins, Eric Prestbo, Gabe Eiras
Tekran Instruments Corporation, Toronto, Ontario, Canada

Introduction:

Methylmercury (MHg) is a widespread environmental concern due to health impacts caused by bioaccumulation of MHg in humans and other top-level predators. With the increasing prominence of MHg research, automated techniques are important to manage the large sample loads generated by ecological studies. Manual analytical techniques require skilled analysts for production of high-quality data and also require substantial time commitments due to labor intensive procedures. Tekran Research and Development crafted the Model 2700 Automated Methylmercury System to provide researchers an adaptable and efficient tool to quantify MHg in environmental samples using EPA Method 1630. The Tekran Model 2700 system utilizes in-vial purging, Hg species capture on Tenax sorbent column, separation utilizing temperature ramped oven and capillary GC column, pyrolytic breakdown to elemental Hg, and quantification by CVAFS. As cutting-edge science often diverges from standard analytical techniques, researchers require instrumentation capable of adaption to custom applications. Below are unique configurations and customizations of the Tekran 2700 currently being used by researchers.

2700 MHg Detection with Species Separation



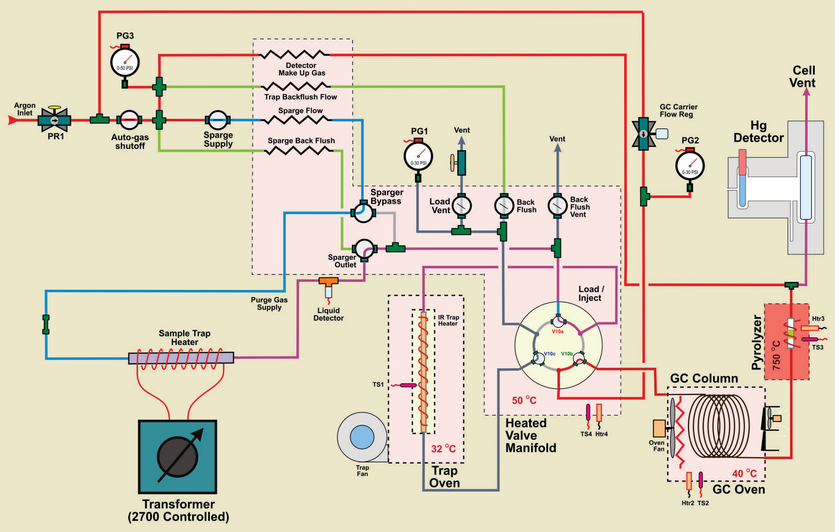
In an effort to better understand methylmercury (MHg) bioaccumulation, researchers endeavor to maximize information collection for each sample. Increasingly common is coupling the Tekran 2700 instrument to a secondary piece of instrumentation such as an ICP-MS to gather isotopic information. The ICP-MS is used successfully with the 2700 as an alternative detection system for MHg quantification. If ICP-MS isotopic fractionation or "fingerprinting" is also desired, mass enrichment is required for accurate characterization of low-level samples. Tekran was contacted by Dr. William Landing[1], Dr. Vincent Salters[1], and Dr. Vincent Perrot[1] of Florida State University to help develop a research tool to overcome this limitation.

In order to accurately quantify isotopic fractionation in samples, trace-level ICP-MS instruments require introduction of approximately 5 ng Hg. Further, it is greatly preferred to introduce a constant solution to the ICP-MS rather than sending a pulse of Hg from the GC directly to the ICM-MS mass detector. By adding programmable post-cuvette outlet ports to the 2700 detector, Hg species are channeled selectively to external trapping solutions. Trapping media concentrations are enriched by running multiple aliquots of the same sample and selectively trapping each species.

Tekran customized the 2700 by adding controllable valves to automatically deliver each mercury species to a unique sample outlet port. After determining exact time of elution, valve timing is synchronized with species elution interval. Work from this project will be presented at a future conference.

- Precise separation of mercury species with capillary GC and programmable GC furnace
- Control of valve timing provides post detector selective trapping of mercury species
- Analyte enrichment makes isotopic analysis by ICP-MS achievable for low-level samples

2700 DMHg Configuration w/ External Cartridge Heater



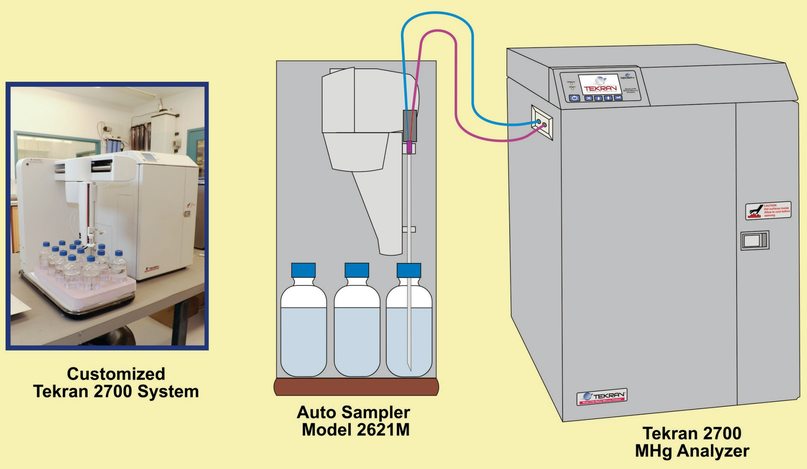
The Tekran 2700 is able to separate and quantify any unique mercury species. Unlike MHg, some organic mercury compounds in the environment do not require pre-treatment prior to analysis. Tekran was contacted by Dr. Joachim Kuss[2] with the Leibniz Institute for Baltic Sea Research to assist with development of a research tool for investigating dimethylmercury (DMHg) production in seawater. An instrument was required for an ocean-bound cruise to perform near real-time analysis of DMHg and MHg in seawater. The capabilities of the 2700 were well-suited to the project requirements.

While fully automated DMHg analytical schemes were presented and discussed, it was determined that a manual sample introduction scheme was the most reasonable approach. Dimethylmercury concentration in seawater are typically in the pg/L range in the open ocean. Using a 20 L equilibrator bottle with an aspirator head, DMHg species are purged from the headspace and focused onto a custom Tenax™ trap.

The Tekran 2700 sample introduction loop was modified to include a manual desorption device. Using the Tekran 2030 Sampler Cartridge Heater (typically used for natural gas sampling) as a starting point, new heaters were developed for easy insertion of the customer's Tenax™ sample traps. The device was further modified to allow faster heating, active cooling, as well as providing remote triggering and control by the Tekran 2700 software interface. For further information about Dr. Kuss's work, refer to poster: *Quantification of the oceanic mercury source - An Overview of Atlantic mercury emission measurements.*

- Dimethylmercury configuration supports direct desorption of manually collected traps
- Technique only requires simple external heating device for automated quantification
- The Tekran 2700 can now support analysis of any manually collected organic mercury species

2700 MHg Large Volume Processing



Sample concentrations for MHg in pristine seawater are generally below quantifiable levels with standard instrumental configurations. Researchers are left with options to: 1) Increase the instrumental sensitivity, 2) Increase the sample process volume, and 3) Pre-concentrate the sample to enrich native analyte levels. Tekran was contacted by Dr. Carl Lamborg[3] with the Woods Hole Oceanographic Institute (WHOI) to help tackle the issue of boosting instrumental performance.

The Tekran 2700 standard method is designed to process 30 mL samples, thus efforts were undertaken to increase the analytical process volume. In order to meet the experimental requirements, sample volumes of 180 mL were necessary. Tekran constructed autosampler racks to support 250 mL septum bottles, making sure the rack layout was supported by the autosampler firmware. Extensive method testing was required to optimize for the new process volume of 180 mL, including adjusting the purging flow rate and sample process intervals. With these custom modifications, the Tekran 2700 analyzer can effectively achieve an instrument detection limit of 0.0003 ng/L.

Sample process time is greatly improved by direct ethylation of seawater samples using ascorbic acid pre-treatment prior to the derivatization. The combination of increased sensitivity and fast process time make the system much more appealing for near real-time shipboard measurements. For further information about this WHOI project, refer to the poster: *Ascorbate-assisted direct ethylation of monomethylmercury from small volume seawater samples* by Kathleen Munson.

- Increased sample process volume improves instrument detection limit by 6X
- Low-level seawater samples analyzed by direct analysis – no distillation required
- Technique only requires simple sample rack modification and customized method event timing file

Tekran 2700 Application Survey						
	Matrix			Analyte		Other Applications
26 Users	Waters	Soil/Sed	Biota	MHg	DMHg	Large volume analysis, isotope analysis, snow & ice, food testing
TOTAL	**20**	**7**	**13**	**26**	**3**	**8**

Tekran polled our customers to determine how the 2700 MHg Analyzer was being utilized. Above is a summary table of the 26 users who responded to our questionnaire.

Tekran 2700 Ongoing Research		
Institution	**Areas of study**	**Analytes**
Florida State University (Landing)	Waters; Species Separation and Isotopic Fractionation	MHg
Woods Hole Institute (Lamborg)	Sea Water; High Volume Processing	MHg, DMHg, Hg^0
Princeton University (Schaefer)	Waters, Sediments; MHg Bacteria Incubation Studies	MHg
University of Western Ontario (Branfireun)	Waters, Biota, Soils; with ICP-MS	MHg
Peking University (Langbo)	Soil, Hair, Urine	MHg
University of Alberta (St. Louis)	Waters, Sediments, Soils; with DRC ICP-MS	MHg
Tsinghua University (Shuxiao Wang)	Soil, Plants, Hair	MHg
University of Minnesota (Nater)	Water, Solids, Biota; Extraction/Distillation Hybrid Preparation	MHg
University of Montreal (Amyot)	Waters, Biota	MHg
Tibetian Research Institute (Qianggong)	Waters, Ice Cores, Snow.	MHg
Liebnitz Institute (Kuss)	Sea Water	DMHg, MHg, Hg^0
University of Connecticut (Balcom)	Waters, Sea Water, Sediment; High Volume Processing, with ICP-MS	MHg

Due to the limitations of this poster format, only selected research applications could be presented. The above table lists other active on-going research applications with the Tekran 2700 MHg Automated Analyzer.

Conclusions:

The Tekran 2700 MHg analyzer provides an exceptionally sensitive and stable platform for performing automated analysis of organic mercury compounds in environmental samples. The system has proven itself to be very adaptable to a diverse range of applications. The 2700 is the instrument of choice for unique organic mercury research applications for the following reasons:

- The Tekran 2700 offers a great degree of expandability with multiple hardware control inputs
- Precision species separation and quantification facilitate cutting edge research
- TekMDS 2.0 software offers complete access to event timing for method customization
- Tekran engineering team has unique ability to customize the analyzer for unique applications

Acknowledgements:

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- [1]Dr. William Landing, Dr. Vincent Salters and Dr. Vincent Perrot with Florida State Univ., Tallahassee, Florida, 32306, USA
- [2]Dr. Joachim Kuss with Leibniz Institute for Baltic Sea Research, Seestrasse, 15 Rostock, D-18119, Germany
- [3]Dr. Carl Lamborg with Woods Hole Oceanographic Institute, Mailstop 51, Woods Hole, MA 02543, USA
- We would also like to acknowledge the many researches who responded to our inquiries for this poster