

Introduction to Automated Chemistry Analyzers – FS3700

APRIL 22ND, 2020



FS3700 Training

Automated Chemistry Analyzers – FS3700 What we will cover today:

- Why the need for testing
- Why the need for Automated Chemistry Analyzers
- What is an Automated Chemistry Analyzer
- History of ACA, Alpkem and OI Analytical





We are one of the world's leading water technology companies





Bringing together the most progressive brands





Xylem Analytics Breakdown





OI History

O.I. Corporation, dba OI Analytical, has been in the analytical instrumentation business for over five decades. Since 1963

OI, a U.S. public company, was purchased in November 2010 by ITT. (Oceanography International) ITT splits into three major parts in October 2011, with the principal water businesses becoming Xylem Inc.

Integration (Royce and GWI) and US distribution (WTW/SI Analytics/B+S) in 2010-2014 Gerhardt 2016



OI Analytical Offers a "World of Solutions" OIA Technology Platforms



Presenter – Hank Hahn

I am currently the OI Analytical Senior Sales Specialist based in College Station, Texas. I have nearly 30 years of analytical instrumentation experience, including product lines for gas chromatography, automated flow chemistry and TOC analyzers. My sales colleagues refer to me as a valued resource, provide wealth of knowledge in not only my understanding the technical side of our instrumentation, but I also have an understanding how it best provides solutions for various applications in numerous industries.







Why the need for Automated Chemistry Analyzers



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- Why do environmental laboratories, municipal and industrial facilities do environmental testing?
 - Commercial laboratories analyze samples for a profit.
 - Municipal laboratories analyze for process control and to satisfy permit.
 - Industrial facilities test to meet permits.
- Environmental testing labs run methods, not instruments.
 - Methods are a prescription, the method defines:
 - MDL
 - Calibration range
 - QC acceptance criteria
 - Extraction/Preparation
 - Instrument
- Most importantly our customers are looking to buy an instrument with ability to run the method



Regulations in depth:

The U.S. EPA is commissioned by the Safe Drinking Water Act and the Clean Water Act to develop routine methods for the analysis of drinking water and wastewater, respectively. Results of these methods are used to establish whether water is safe to drink or if an industrial or municipal effluent is in compliance with a permit.

https://www.epa.gov/sdwa

https://www.epa.gov/laws-regulations/summary-clean-water-act

Title 40: Protection of Environment Part 136 – Guidelines establishing test procedures for the analysis of pollutants.

https://www.ecfr.gov/cgi-bin/text-

idx?SID=705af9d3f7e2446f577678b71f4687a8&mc=true&tpl=/ecfrbrowse/Title40/40cfr136_m ain_02.tpl

The NPDES permit program addresses water pollution by regulating point sources that discharge pollutants to waters of the United States.

https://www.epa.gov/npdes



Regulations in depth:

ASTM Committee D:19 -The study of water, the promotion of knowledge thereof, and the standardization of terminology methods for: Committee

* Sampling and analysis of water, waterborne materials, and wastes, water formed deposits and fluvial sediments,

* Surface-water hydraulics and hydrologic measurements,

* The determination of the performance of materials or products used to modify water characteristics, and

* The determination of the corrosives or deposit forming properties of water.

The term "water" includes, but is not limited to, surface waters (rivers, lakes, artificial impoundments, runoff, etc.), groundwater and spring waters, wastewaters (mine drainage, landfill leachate, brines, waters resulting from atmospheric precipitation and condensation (with the exception of acid deposition), process waters, potable waters, glacial melt waters, steam, water for subsurface injection and water discharges including waterborne materials and water-formed deposits.

https://www.astm.org/

Standard Methods: For the Examination of Water and Wastewater https://www.standardmethods.org/ SM4500 Series



Safe Drinking Water Act: Consumer Confidence Reports (CCR) – College Station http://www.cstx.gov/index.aspx?page=822





Monitoring – Nitrates/Nitrites

BACKGROUND ON NITRATES

Nitrate is a water soluble molecule made of nitrogen and oxygen. It is formed when nitrogen from ammonia or another source combines with oxygenated water. Nitrate is naturally found in plants and many foods, and is tasteless and odorless. Since it does not evaporate or bind well to soil, it is used by plants or stays in the water. Nitrate reactions can cause oxygen depletion in water, which may cause fish kills.



SOURCES OF NITRATES

Nitrates are in fertilizers, animal waste, human sewage, decaying plant debris, and industrial waste.

HEALTH CONCERNS

Causes "blue baby syndrome" as nitrate changes to nitrite in their stomachs Pregnant women should not drink if contaminated, people with heart or lung disease, inherited enzyme defects, or cancer are more sensitive. Causes "brown blood disease" in fish.



ACA Markets/Customers

Application	Market	Customer (s)
CN	Environmental, Industrial Plating, Gold Milling	Commercial laboratories, POTW (Publicly Owned Treatment Works), Drinking water, Industrial labs, and gold mills
Phosphorus (TP, PO4)	Environmental	Commercial, POTW (Publicly Owned Treatment Works), university, agriculture, federal, state, county, and local, and industrial laboratories
Nitrogen (NO2, NO3, NH3, TKN)	Environmental	Commercial, POTW (Publicly Owned Treatment Works), university, agriculture, federal, state, county, and local, and industrial laboratories
Phenol	Environmental	Commercial, POTW (Publicly Owned Treatment Works), university, agriculture, federal, state, county, and local, and industrial laboratories



Industry/Market Segments using ACA/CFA Methods

Drinking Water Facilities

About 52,000 public water systems in the United States. These facilities treat surface water to potable water quality. Need to test source water and finished water by EPA approved methods to ensure compliance with regulation and process control.

Contaminant	Method	Maximum Contaminant
		Level (mg/L)
Cyanide (free)	OIA-1677	0.2
Nitrate + Nitrite Nitrogen	EPA 353.2	10
Nitrite Nitrogen	EPA 335.2 no cadmium	1
	reduction	
Orthophosphate	EPA 365.1	N/A

Wastewater Facilities

About 16,000 publicly owned treatment works (Publicly Owned Treatment Works),) In the United States. These facilities treat wastewater to remove harmful pollutants making water safe to the environment. EPA regulates all POTWs by issuing them a permit (NPDES).

Non POTW Facilities (Refineries, Chemical Plants, Metal Plating, Power Plants)

Nearly 95,000 facilities in the United States. These facilities are issues a NPDES permit as they discharge into navigable streams. Monitor water in the plant and water discharged from the plant.



Industry/Market Segments using CFA Methods

40 CFR Part 136 analytes and methods often required on NPDES Permits

<u>CONTAMINANT</u>	METHOD
Ammonia Nitrogen	EPA 350.1
Nitrate + Nitrite Nitrogen	EPA 353.2
Orthophosphate	EPA 365.1
Total Phosphorus	EPA 365.1 or EPA 365.4
Total Kjeldahl Nitrogen	EPA 351.2
Total Phenolics	EPA 420.4
Total Cyanide	ASTM D7511



Industry/Market Segments - NPDES

The Clean Water Act prohibits anybody from discharging "pollutants" through a "point source" into a "water of the United States" unless they have an NPDES permit. The permit will contain limits on what you can discharge, monitoring and reporting requirements, and other provisions to ensure that the discharge does not hurt water quality or people's health.



Example: Total Cyanide and Available Cyanide purchase.

Petrochemical facility in the Houston Ship Channel farming samples to local water authority awaiting results of did their properly treat their wastewater. Performed demo for Total and Available Cyanide, purchased a system where they can test immediately get results.



Industry/Market Segments using CFA Methods

Environmental/Contract Laboratories

Commercial labs analyzing samples on a contract or a for pay basis. These laboratories perform analysis for the afore mentioned segments that out source their sampling. These sites operate under regulatory approval of methods and strict quality control guidelines.

<u>CONTAMINANT</u>	<u>METHOD</u>
Ammonia Nitrogen	EPA 350.1
Nitrate + Nitrite Nitrogen	EPA 353.2
Orthophosphate	EPA 365.1
Total Phosphorus	EPA 365.1 or EPA 365.4
Total Kjeldahl Nitrogen	EPA 351.2
Total Phenolics	EPA 420.4 / 420.2
Available Cyanide	OIA 1677 / D6888
Total Cyanide	ASTM D7511



ISO Methods

ISO/TC 147 Water quality

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Contaminant	Method
Cyanide (Free)	ISO Method 14403
Cyanide (Total	ISO Method 14403
MBAS	ISO Method 16265
NO2/NO3 in Milk	ISO Method 14673



Environmental Testing



Nitrogen and phosphorus account for about 80% of the analytes measured by ACA. Well over ½ of these analyses are for the simple nutrients ammonia, nitrate+nitrite, and phosphate. The remainder is total nitrogen and phosphorus either by the Kjeldahl or persulfate digestions.



Precious Metal Extraction, Plating, Petro & Chemical



Gold is extracted from ores using cyanide solution. The gas diffusion amperometry methods for free, available, and total cyanide were developed because they are the only methods known capable of accurate determination of cyanide in these matrices. Offer both laboratory and on-line devices.



Tobacco



Methods developed for quality control testing of tobacco products.





Why automation



Why Automation?

The purpose of these analyzers is to <u>automate</u> wet chemical analysis; To exactly reproduce reagent addition, reaction time/ mixing, and measurement time.

Currently these labs maybe using: ISE, Spectrophotometer and Titration all manual Interaction.

Several "types" are available:

- Segmented Flow Analyzers (SFA)
- Flow Injection Analyzers (FIA)
- Discrete Analyzers





Why Automation?

Save time Decrease cost Improve quality Reduce waste

Automation is having a machine do things for you releasing you from repetitive tasks and allowing your laboratory to analyze more samples per day and at the same time, improve long term method performance. Anyone looking to increase throughput, and increase overall laboratory capacity should consider some form of automation.

Extra benefits include waste minimization and decreased costs. If you are looking to increase your labs efficiency then you should consider automation.



The benefits of automating wet chemical analysis

Do more samples, gone are: Pipetting, reading colorimeters and Ion Selective Electrodes

More samples per day means more profit Environmental labs exist to make a profit.

Water treatment facilities and labs at industrial facilities that do not charge per test will still profit by letting the instrument do the work for them.

An automated instrument lets you gather more information and keeps working multiple shifts and overnight. It is feasible to accomplish three times the work than you could do manually in an 8 hour day.



The benefits of automating wet chemical analysis

Almost any method that can be done manually can be automated. Regardless of the automation technique they all do the same thing. And that is make the lab analyst life easier.

Manual methods are by nature error prone because analysts get tired, or because pipeting, mixing, and so forth just varies between analysts.

Manual methods limit a laboratory's ability to do more samples per day. An analyst must stand at the machine to record every measurement.

Automation equates to: Better results

Lower cost per test



Laboratory costs that can be reduced by automation

	Laboratory Cost
Direct labor	20 – 28 %
Indirect Labor	7 – 12 %
Operational Supplies	10 – 20 %

At labs most expensive cost is labor, and after that supplies.



The benefits of automating wet chemical analysis another spin....

Flow analysis has advantages over manual methods that include smaller sample volume and reagent consumption, greater reproducibility, and higher throughput. Typical continuous flow methods can analyze samples from 30 up to over 100 samples per hour. Normally, throughput is limited to 30 – 90 samples per hour to allow baseline resolution between samples, better detection limits, and a larger calibrated range. Since continuous flow methods (SFA and FIA) analyze every sample and standard at exactly the same time following injection into the continuously flowing stream reactions do not need to be brought to equilibrium (steady state).



Continuous Flow Analysis (CFA)

• Analysis technique in which the sample becomes a part of a flowing stream where operations take place as the sample is carried from the injection point to a flow-through measuring device, and then to waste.

Segmented Flow Analysis (SFA), Flow Injection Analysis (FIA)

Analyte

• The specific substance being identified or measured in an analysis.

Accuracy

• The extent to which a measurement approaches the true value of the measured quantity.

Baseline

• The steady transmittance level appearing on the detector display when liquid flows through the flow cell.



Some Terminology cont.

Calibration Curve

 A graphical representation obtained when a concentration versus voltage or peak height output curve is prepared for any number of standards or calibrants.

Carryover

• Sample-to-sample interaction.

Detector

• Measures absorbance fluctuations of the analytical stream resulting from color development as the reagent and analyte react. On the Photometric detector, the output is a digital response proportional to the absorbance.

Flowcell

• A flow-through optical cell that allows light absorbance to be measured on a continuously flowing liquid stream.

Flow rate

 The volume of liquid flowing past a point per unit of time. Normally measured in milliliters per minute (mL/minute) or microliters per minute (µL/minute).



Some Terminology cont.

Heater

• Heats the analytical stream to a specified temperature.

Injection Valve

• The eight-port Injection Valve regulates the volume of samples introduced into the FS3700 system.

Interference filter (photometer)

• The interference filter separates the light wavelength that enters the detector before the light passes through the analytical stream.

Linearity

• The degree of proportionality between peak height and analyte concentration.

Mixing coil (Analytical Cartridge)

• A series of loops or turns on a cartridge that create mixing action and allows a time delay needed for a chemical reaction.



Method Detection Limit (MDL)

• The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

Minimum Level of Detection (ML)

• The level at which the entire analytical system will give a recognizable signal and acceptable calibration point, taking into account method specific sample and injection volumes.

Precision Pump

• A pumping system that moves liquids by compressing flexible tubing between a solid surface (platen) and a roller. Since the flexible tubing contains the liquid, no contact occurs with the pump mechanism.

Precision

• The degree of mutual agreement among data that have been collected in the same manner.



Pump tube

 Calibrated plastic tubes installed in the pump platens and stretched across the pump rollers. They deliver samples, reagents, and air to the Analytical Cartridge. The flow rate of the pump tubes depends on the tube's internal diameter and the pump speed. The color-coded shoulders on each tube identify the internal diameter of the pump tubes.

Relative Standard Deviation (RSD)

• A statistical measure of precision in which the deviation of multiple measurements are expressed relative to the average value of the measurements.

Reagent Blank

• An aliquot of reagent water or other blank matrix the is treated like a sample.



Reagent

• A chemical substance or material that aids in or creates a specific chemical reaction.

Reagent Blank

An aliquot of reagent water or other blank matrix the is treated like a sample.

Relative Standard Deviation (RSD)

 A statistical measure of precision in which the deviation of multiple measurements are expressed relative to the average value of the measurements.

Sensitivity

• The ability of a method to discriminate between small differences in analyte concentration.





What is an Automated Chemistry Analyzer and Techniques



An Automated Chemistry Analyzer

The purpose of these analyzers is to <u>automate</u> wet chemical analysis; To exactly reproduce reagent addition, reaction time/ mixing, and measurement time. Several "types" are available:

- Segmented Flow Analyzers (SFA)
- Flow Injection Analyzers (FIA)
- Discrete Analyzers



What is an Automated Chemistry Analyzer?

A continuous flow analyzer consists of a pump that moves reagents through a manifold composed of tubing with tees for the addition of reagents, sample, and coils for mixing sample, plus reagent, and creating time delays that allow reactions to proceed.

How the sample volume is measured and injected into the tubing is a primary differentiator between SFA and FIA, the two major divisions in continuous flow analysis. **SFA uses air segmentation to separate sample segments** allowing for better mixing and decreasing carryover between sample segments. **FIA does not segment with air** and relies on the dispersion that occurs within the tubing to mix the sample. Since there is no air segmentation, FIA chemistries proceed rapidly through the cartridge.



Principles of ACA Flow Mix React Detect



The OI Analytical Flow Solution

The Flow Solution applies continuous flow, continuous flow refers to samples aspirated, reagents are added, a color producing reaction occurs, concentrations are measured and results are processed – all in a continuous flow.

The Flow Solution uses both segmented (SFA) and flow injection analysis (FIA) techniques.



The OI Analytical CNSolution

CN Solution involves injection of sample into a carrier stream, once injected the sample is segmented and acidified to release hydrogen cyanide (HCN) which passes through a hydrophobic membrane. HCN is absorbed in acceptor solution and directed through a flowcell where the cyanide is measured amperometrically at a silver working electrode.



What is an Automated Chemistry Analyzer?

An example of Segmented Flow Analysis:

Sample aspirated from sample cup, pumped into the analytical plate where segmentation and mixing with reagents. Air bubbles are injected as sample progresses through system can be heated to create desired chemical reaction. Since process might be long air segmentation serves to minimize sample zone dispersion/carryover. Chemical reactions results in a color which is pumped through the flow-cell in the detector and measured with nanometer filter and processed into software (FlowView).



What is an Automated Chemistry Analyzer?

An example of Flow Injection Analysis:

In flow injection analysis, a precise amount of sample is injected into the continuously flowing carrier stream by an injection valve Reagents added and it may be heated for desired chemical reaction as well. Reaction occurs and color is measured same as with the segmented process.



Analytical Techniques of ACA

Automated Wet Chemistry



Analytical techniques available include flow injection analysis, segmented flow analysis and injection segmented flow analysis



Segmented Flow analysis is the first auto chemistry. Segmented flow enjoys over 50 years of success as a proven technology. Segmented flow is the basis of multiple automated EPA and other regulatory methods.







Samples are pumped into a continuously flowing stream of reagents that is segmented by air, or another inert medium. The segmentation limits dispersion allowing reactions to proceed to equilibrium, or maximum color development. The first automated wet chemistry analyzer was a segmented flow analyzer. Most automated EPA methods were written for segmented flow.



All Segmented Flow Analyzers separate sample slugs from each other by "air" bubbles. The bubbles limit transfer of one sample segment to the next as the samples travel down the path of the tubing. The segments allow sample solutions to travel slower through the tubing giving them extra time to completely react with reagents.



Gas

Gas





As the segmented flow sample travels through mixing coils the end over end action that happens inside the coils ensures 100% mixing of sample with reagent. 100% mixing also guarantees a maximum number of collisions between analyte and reagent. The analyte reacts with the reagent by colliding with it. The idea is to make sure that all possible reactions occur producing maximum color product for measurement by the detector.





Prior to entering the flow cell, the segmentation gas is removed from the stream using a debubbler.

The non-segmented stream then flows into a flow cell designed for colorimetric detection, an interference filter of appropriate wavelength is required.



SFA Peak (Ammonia/TKN)



SFA peaks have a slight flat top which represents approximately 95% of reaction completion to provide the highest sensitivity. SFA increases throughput because less wash is required between sample segments. A flat top on the peak guarantees that all reagent and analyte have reached maximum reaction.



Benefits of Segmented Flow:

- Low MDL
- Excellent Precision
- Steady state reactions
- Limited dispersion



Flow Injection Analysis



Flow injection analysis uses dispersion by injecting a sample into an unsegmented carrier stream, adding one or more reagents, mixing, heating, reacting and detecting using continuous flow.



Flow Injection Analysis



FIA can be used for higher sample throughput of chemistries and uses shorter reaction times as the chemistry does not need to be brought to completion due to the highly reproducible injected sample volumes and reaction times.



FIA Peak



Since the reaction is not brought to completion, FIA peaks do not have flat tops and are nearly Gaussian in shape.



Flow Injection Analysis

Flow Injection Benefits:

- Rapid Analysis
- No need for Debubblers
- Excellent Precision
- High throughput
- Recommended for those new to Automated Chemistry Analyzers



Injection Segmented Flow Analysis (iSFA) NO2/NO3 and Total CN D7511 Chemistries



Injection segmented flow uses FIA to inject a highly reproducible sample volume then segments the carrier stream with air bubbles followed by reagent addition, heating, mixing and detection.



Injection Segmented Flow Analysis (iSFA)



iSFA uses FIA to inject a highly reproducible sample volume then segments the carrier stream with air bubbles followed by reagent addition, heating, mixing and detection. iSFA is used for chemistries requiring turbulent mixing such as nitrate where the sample and the ammonium chloride buffer carrier stream must be rapidly reacted with the walls of an open tubular cadmium reactor to reduce nitrate to nitrite and within the UV Lamp with the Total CN

a xylem brand

Injection Segmented Flow Analysis (iSFA)

Nitrate Coil Reaction Dynamics





The turbulent mixing generated by segmented flow actively moves the nitrate ions at the center of the sample zone out to the walls of the copperized cadmium coil to enable rapid and efficient reduction to nitrite.



Injection Segmented Flow Analysis (iSFA) Peak



iSFA peaks look like FIA peaks since the sample is injected and the reaction is not brought to completion.



SFA and FIA Techniques on the same instrument....

OI Analytical Flow Analyzers care capable of SFA and FIA on the same instrument Offers:

- User flexibility
- Modular design
- Increase capability





History of ACA, Alpkem and Ol Analytical



Flow Analyzers - History

The AutoAnalyzer is an automate analyzer using a flow technique called continuous flow analysis (CFA), first made by the Technicon Corporation. The instrument was invented in 1957 by Leonard Skeggs, PhD and commercialized by Jack Whitehead's Technicon Corporation. The first applications were for clinical analysis, but methods for industrial analysis soon followed. The design is based on separating a continuously flowing stream with air bubbles.

Flow injection analysis (FIA), was introduced in 1975 by Ruzicka and Hansen, The first generation of FIA technology, termed flow injection (FI), was inspired by the AutoAnalyzer technique invented by Skeggs in early 1950s.While Skeggs' AutoAnalyzer uses air segmentation to separate a flowing stream into numerous discrete segments to establish a long train of individual samples moving through a flow channel, FIA systems separate each sample from subsequent sample with a carrier reagent.



Flow Analyzers - History

Hudson and Ruzicka took their idea to a company Bifok (Teactor, a Perstop company) and Tecator became the first company to commercialize FIA. Today OI and formerly Lachat are the primary provider of FIA.

Micro-Continuous Flow Analysis (RFA-300)

In 1984 first micro segmented CFA system was introduced to the industrial laboratory by Alpkem.

Simultaneous FIA and Segmented Flow

In early 1990's continues its development and introduced the first instrument that allowed both FIA and Segmented flow to be run simultaneously. This instrument was the Flow Solution 3590

In 1992 ALPKEM introduced the Flow Solution Analyzer (FS III) then followed with FS3000 (1996) and Flow Solution IV in (1997).



Flow Analyzers - History

In 1996, OI purchased Alpkem, a subsidiary of Perstorp, providing continuous flow capability. Tecator, the analytical arm of Perstorp, was a pioneer of Flow Injection Analysis (FIA) in Europe since the early 1970's and Alpkem had introduced the first third generation Segmented Flow Analyzer (SFA) as early as 1983. The combination made OI Analytical the only continuous flow analyzer company that provides both SFA and FIA.



OI Analytical ACA



FS3000 introduced 1995, compact easy to use advancement in automated ion analysis. Combined FIA and SFA on same platform.



CN Solution introduced 1995 designed from the Model 3202 which was introduced and designed for precious metal mining industry. CN (CATC / WAD results in 90 seconds and no distillation!

1999 EPA approved OIA1677 which removed distillation step with gas diffusion



OI Analytical ACA



Flow Solution IV introduced in 1997, Ion Analysis...Beyond the limits!

Advanced ER Detection – single calibrations covering 3 to 4 orders of magnitude.

Productive with high throughput

Flexible with choice of either FIA, SFA or both

simaltaniously.

Expandable to 6 channels.

WinFlow software



OI Analytical ACA



CN3100 Introduced 2005, single or dual channel. Dedicated to Available Cyanide and Total CN analysis. Utilization of UV Digestion for Total CN. Used to break down all the strongly bonded CN.

2012 EPA approves ASTM D7511 which finally removed distillation step from Total Cyanides



FS3100 Introduced 2006, Versachem cartridge with snap on and off chemistries, 2 channels of FIA and 3 channels of SFA.

2012 EPA approves Gas Diffusion with Ammonia/TKN

Introduction of CETAC XYZ Autosamplers 90 and 360 positions.





Thank you for joining us today! For more information, please contact Hank.Hahn@Xyleminc.com info.apac@xyleminc.com



Part 2 - Automated Chemistry Analyzers May 1st 9AM (SNG)

TOC Analyzers April 30th 9AM (SNG)

www.Xylem-Analytics.asia www.Xylem-Analytics.in www.Xylem-Analytics.com.au

