ULTRA-PURE WATER MONITORING FOR COGEN APPLICATIONS
(Conductivity or NDIR Detection?)

THE PROBLEM:

For maximum protection of turbines and other costly hardware in a power plant, conductivity detection cannot be reliably used.

LIMITATIONS OF CONDUCTIVITY DETECTION:

For reasons described in subsequent paragraphs, conductivity cannot be reliably used if the following species are present in the sample OR FORMED BY THE OXIDATION PROCESS:

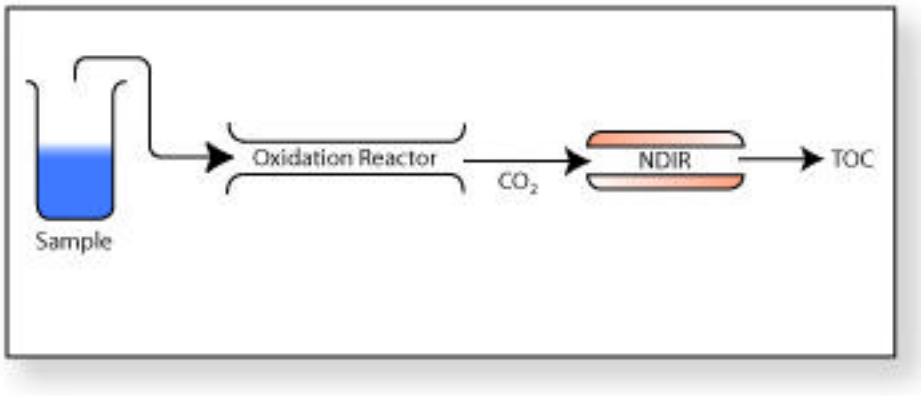
INTERFERING SPECIES

Acid Gases	Iodine
Organic Acids	Hypochlorous Acids
Halogenated Organics	Nitrite Ions
Sulfide Ions	Other Ions with Dissolved Gas Phases

ADVANTAGES OF ALTERNATE NON-DISPERSIVE-INFRARED DETECTION (NDIR)

NDIR detection of the CO_2 gases formed in the oxidation process has no interferences.

DISCUSSION



In Total Organic Carbon (TOC) analysis, the sample is generally oxidized in a reactor where carbon is directly converted to CO_2 gas and other chemical species are converted to their respective oxides. Thus, the CO_2 detector must be specific to CO_2 gas ONLY, which is in proportion to the carbon present in the sample and provides a direct correlation to TOC.

SOME EXAMPLES OF CONDUCTIVITY INTERFERENCE

For purposes of clarity, the other factors having significant effect on conductivity measurements will not be covered. These factors include:

Temperature

PH

Differential Measurement Errors

Calibration

Membranes (if used)

EXAMPLE #1 – ORGANIC ACIDS

A sample contains 1,250 parts-per-billion per liter (ppb/l) of acetic acid (CH_3COOH) or 500 ppb/l of TOC. The original unoxidized acetic acid is generally

ionized and this sample would have an equivalent conductivity of 4.8 µS/cm (at 25°C).

When acetic acid is oxidized to CO_2 and water, the equivalent conductivity is 1.71 µS/cm. Thus the output of the conductivity detector is –3.09 µS/cm (1.71 µS/cm – 4.8), which is obviously a gross instrumental error. Most manufacturers of this approach default all negative readings to "Zero", which could have serious future harmful consequences to equipment. Hidden false negatives are more pernicious than false positives, such as in the next example.

EXAMPLE #2 – HALOGENATED ORGANICS

A sample contains 990 ppb of chloroform ($CHCl_3$) equivalent to 100ppb of organic carbon. Chloroform is oxidized to CO_2 and hydrochloric acid (HCl), which dissociates to H^+ and Cl^- ions. The oxidized chloroform sample conductivity is approximately 10 µS/cm.. This is a significant error of about 900%, as the CO_2 contribution should only contribute about 1 µS/cm.

TECHNIQUES TO LESSEN CONDUCTIVITY INTERFERENCES:

The use of membranes to block some conductivity interferences prior to measurement has had only limited success.

It does minimize some ionic interferences but still has serious limitations because other major interferences still exist, such as acid gases and ions with gas phases (sulfides, nitrites, iodine, hypochlorous acids, etc.).

OTHER FACTORS: What About Inhibitors?

Many COGEN operations are like joint ventures, whereby one party generates the energy and the other energy-using party returns pure water from condensate, makeup water, etc. to the generating party to be used as boiler feedwater. The returned water must be analyzed for impurities prior to use, with significant financial consequences in many ventures if "out-of-tolerance" conditions exist.

Inhibitors generally contain amines and other organic compounds. By mutual consent, most parties would agree not to consider these for any penalty charged but, until recently, there has been no practical method to eliminate their TOC contribution.

STAR has developed a unique replaceable cartridge to remove inhibitors prior to the measuring stage of the TOC analyzer, which takes them out of the charge-back equation. This technique eliminates potential controversial matters in the future by clearly defining boundary conditions related to sources of organic contamination.

CONCLUSION:

Because of many interferences, conductivity detection of the CO_2 gases generated in TOC analysis cannot provide a true measurement of TOC.

NDIR offers the only practical non-interference approach to CO_2 measurement and can thus provide a TRUE analysis of TOC.

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