PUB 0053

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Determination of Trace Organic Impurities in Semiconductor Processing Chemicals

by

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Presented at Microcontamination Conference
October 1991, San Jose California

DESCRIPTION OF ANALYTICAL METHODS

An OI Analytical OI-700 TOC analyzer was modified for these studies. In its standard configuration which is used for monitoring water TOC levels, a water sample is acidified and heated to 100°C to remove inorganic carbon (carbonate, bicarbonate, and CO_2). In a subsequent step, sodium persulfate is added to oxidize all organics to CO_2. The CO_2 is collected on a molecular sieve trap, then the trap is rapidly heated to desorb the CO_2. The CO_2 is quantitated using a non-dispersive infrared (NDIR) detector. This method has few interferences, a good detection limit (about 0.004 mg/L), and a large linear range (typically 0-5 mg/L for a 10 mL sample).

To allow use with corrosive acids, the OI-700 was modified with plumbing changes that allow it to handle more viscous and corrosive solutions. A scrubber system was installed that allows removal of corrosive or potentially interfering gases that might damage the infrared detector. For each chemical, optimization of the instrumental parameters, use of selected oxidants and specific sample pretreatments were required to obtain acceptable recoveries and valid analytical results.

Detection limits for TOC in most chemicals analyzed were in the range of 0.03 - 0.6 mg/L, and most chemicals analyzed had impurities significantly above the detection limits. Typical recoveries of standards spiked into the chemicals are 90-105% and typical accuracy is ±10% for readily oxidizable compounds. A summary of the current detection limits for selected chemicals is given in Table 1.

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SUMMARY

New methods have been developed for the analysis of trace organic compounds in inorganic semiconductor processing liquids. Organic compounds are measured as TOC (Total Oxidizable Carbon). A survey of the TOC levels in selected fluids is presented. Chemicals analyzed include sulfuric acid, phosphoric acid, hydrofluoric acid, ammonium fluoride, ammonium hydroxide, sodium hydroxide and hydrogen peroxide. High levels of organics (TOC > 1 mg/L) are found in many of the chemicals, especially hydrogen peroxide and sulfuric acid.

INTRODUCTION

Trace levels of organic impurities in semiconductor processing fluids can cause disastrous yield losses during semiconductor manufacturing. When organic compounds are present in processing chemicals and wet processing baths, some may adhere to the wafer surfaces as particles or as thin films. Even below monolayer levels, adsorption of organic compounds onto wafer surfaces can dramatically influence the surface wettability. A hydrophobic surface can reduce etch rates and cause uneven etching. Organic films can also affect the growth rates of oxides and result in uneven oxide layers. Rinsing away ionic and metallic impurities from wafers and processing equipment may be ineffective when they are covered by organic deposits. If the organic materials are not completely rinsed away before subsequent processing, organic compounds can get occluded between layers, which can lead to poor adhesion and variable conductivity. It is believed that a thin film of silicon carbide may be formed when organics are trapped at silicon surfaces and subsequently subjected to high temperature processing. For the above reasons, monitoring and controlling organic contaminant levels in semiconductor processing chemicals is needed.

Most semiconductor processing facilities routinely monitor and control their ultrapure water TOC (Total Oxidizable Carbon) levels between 1 and 50 ppb. Due to a lack of analytical methods, the instruments used for deionized water TOC monitoring are not currently suitable for monitoring TOC in chemicals. Hence levels of organic impurities in inorganic chemicals are seldom measured or controlled. We undertook an extensive R&D project to develop new methods for determining TOC in selected semiconductor processing chemicals. Following is a survey of the TOC levels found in typical semiconductor processing fluids.

TABLE I. SUMMARY OF CURRENT DETECTION LIMITS FOR TOC IN SELECTED CHEMICALS

REAGENT Concentrations in weight %	**DETECTION LIMIT (mg/L)**
ACIDS	
SULFURIC ACID, 90-100%	0.2
PHOSPHORIC ACID, 85%	0.1
HYDROFLUORIC ACID, 48-50%	0.1
10:1 DILUTE HF, APPROX 5%	0.03
BASES	
AMMONIUM HYDROXIDE (28-30% NH_3)	0.06
SODIUM HYDROXIDE, 50%	0.4
POTASSIUM HYDROXIDE, 45%	0.6
OTHER CHEMICALS	
AMMONIUM FLUORIDE, 40%	0.1
HYDROGEN PEROXIDE, 30%	0.2
BOE (Buffered oxide etchant) = HF/NH_4F mixtures	0.1 - 0.2

RESULTS

Using the newly developed analytical methods, we have determined the TOC levels in representative semiconductor- or reagent-grade chemicals from multiple vendors. Chemicals analyzed include sulfuric acid, phosphoric acid, hydrofluoric acid, hydrogen peroxide, ammonium hydroxide, ammonium hydroxide and sodium hydroxide. We found high TOC levels (> 1 mg/L) in many of the samples. Some examples of the levels of organic impurities found in our initial screening survey are given in Figures I-VIII and comparisons of the detection limits with the lowest, average and highest TOC levels for each reagent are summarized in Figure IX.

Sulfuric acid, H_2SO_4. Twelve SEMI-grade sulfuric acid samples had TOC levels ranging from 0.2 to 9.1 mg/L. Both the lowest and the highest samples came from the same vendor, demonstrating the large lot-to-lot variations that are currently possible. The lowest TOC sample came from a glass jug, but low TOC samples were also found for samples from plastic jugs. The higher average TOC levels for plastic jugs may suggests that part of the TOC may come the plastic. Long-term testing of identical sulfuric acid samples split between both glass and plastic bottles is needed.

85% Phosphoric acid, H_3PO_4. Ten SEMI-grade phosphoric acid samples from 5 vendors were found to have very similar TOC levels. A 3 year old plastic bottle from Vendor A had higher TOC (1 mg/L) than three newer bottles with TOC = 0.5 mg/L. Interestingly, the highest TOC level was found for the only sample in a glass bottle. Thus, buying reagents in glass bottles is currently no guarantee that they will have lower TOC levels.

49% Hydrofluoric acid, HF. Three samples of SEMI-grade 49% HF from three vendors were analyzed. All samples had TOC significantly above the detection limit and the Vendor C sample had more TOC than Vendors A & B.

10:1 Dilute Hydrofluoric acid, HF. Three lots of 10:1 HF from the same vendor all showed very low levels of TOC. The levels were lower than for the 49% HF.

40% Ammonium Fluoride, NH_4F. Three samples of SEMI-grade NH_4F from three vendors were analyzed. Each was in a plastic bottle that was approximately 2 years old. We believe all bottles were polyethylene. One bottle had discolored to a tan color, and the TOC of the NH_4F in this bottle was 10 times higher than in the other two bottles. This suggests that the TOC may have come from the bottle. Large variations in the amount of organics leaching from bottle are possible, depending on the manufacturer of the bottle.

Ammonium Hydroxide, NH_4OH (28-30% NH_3). Six samples from three vendors were analyzed and significant lot-to-lot variations were found for Vendors B and C. The highest sample had 0.88 mg/L TOC.

50% Sodium Hydroxide, NaOH. Two samples of 50% NaOH from two vendors were analyzed. The TOC for the highest sample was 2.7 mg/L.

30% Hydrogen Peroxide, H_2O_2. Six samples of hydrogen peroxide from 4 vendors were found to all have similar, high levels of TOC. Hydrogen peroxide appears to have the highest average TOC levels of the chemicals tested.

DISCUSSION

Many manufacturers are maintaining the concentrations of metal impurities in their chemicals at or below the ppb level. In contrast, our survey demonstrates that TOC concentrations are two to four orders of magnitude higher. Thus the largest concentration impurities seen by wafers are due to organics. Some organics that are very water soluble may not be very detrimental since they may be removed by deionized water rinses. It is the non-volatile or relatively hydrophobic compounds that are most likely to cause problems since they may adhere to the wafer. The current method measures TOC only and does not discriminate between the types of organic compounds. TOC is however, the most convenient analysis to screen for high organic levels.

Thus far, we have screened the TOC levels for SEMI- or reagent-grade chemicals in reagent bottles from several vendors. The detection limits, lowest, average, and highest TOC levels found for seven of the chemicals are summarized in Figure IX. The apparent conclusions are:

1) Hydrogen peroxide samples have the highest average TOC levels, followed by sulfuric acid and sodium hydroxide.

2) Other chemicals have average TOC levels near 1 ppm, with ammonium hydroxide having the lowest TOC levels.

3) Nearly all the chemicals have TOC levels above the current detection limits.

We suspect that some of the TOC in the reagent grade chemicals comes from the reagent containers, especially if they are plastics such as polyethylene. Studies of the leaching of organics from the containers into the chemical vs. time are needed to define shelf-lives. One old ammonium fluoride sample in a discolored bottle had much higher TOC than samples in newer bottles. The extent of TOC leaching from plastic bottles may be very dependent on the exact source and history of the bottles and on the type of chemical they contain. Some samples in glass bottles have high TOC and some sample in plastic bottles (e.g. 10:1 HF and ammonium hydroxide) have low TOC. Since TOC is not currently controlled by the manufacturers, large variations are possible irrespective of the type of bottle used.

The TOC levels in all the hydrogen peroxide samples analyzed fall in the range 3-10 mg/L. In some cases, some of the TOC might be due to organic stabilizers added to the solution, but most manufacturers claim they add no organic stabilizers. Solvents are used in the production of hydrogen peroxide in the US via the anthraquinone process. The observed TOC may be from the solvents or the degradation of the anthraquinone. To attempt identification of the organic impurities, hydrogen peroxide samples from two manufacturers were extracted with methylene chloride and the methylene chloride extracts were concentrated and analyzed by GC-

MS (gas chromatography-mass spectrometry) under identical conditions. One sample (with TOC = 6 mg/L) showed very little extractable material whereas the other sample (with TOC = 9 mg/L) showed large amounts of extractable organics which might be detrimental to semiconductor processing. Thus samples with very similar TOC levels may have very different organic compound distributions.

Considering that hydrogen peroxide has the highest TOC levels of the chemicals tested, and since hydrogen peroxide is used in several semiconductor processing steps (piranha baths, SC-1, SC-2 and for deionized water system sanitization), reductions in the TOC organic impurity levels may prove beneficial.

We have begun collecting additional data for chemicals at the point-of-use and in some cases, we find much higher TOC levels. For example, TOC concentrations in sulfuric acid vary widely and can be up to hundreds of mg/L in spent sulfuric acid baths. Testing at the point of use should prove especially valuable.

We are currently developing methods for determining TOC in other chemicals including HNO_3, HCl, SC2 ($HCl + H_2O_2$), SC1 ($NH_4OH + H_2O_2$) and piranha baths ($H_2SO_4 + H_2O_2$). Data are being collected for BOE (buffered oxide etchant) samples.

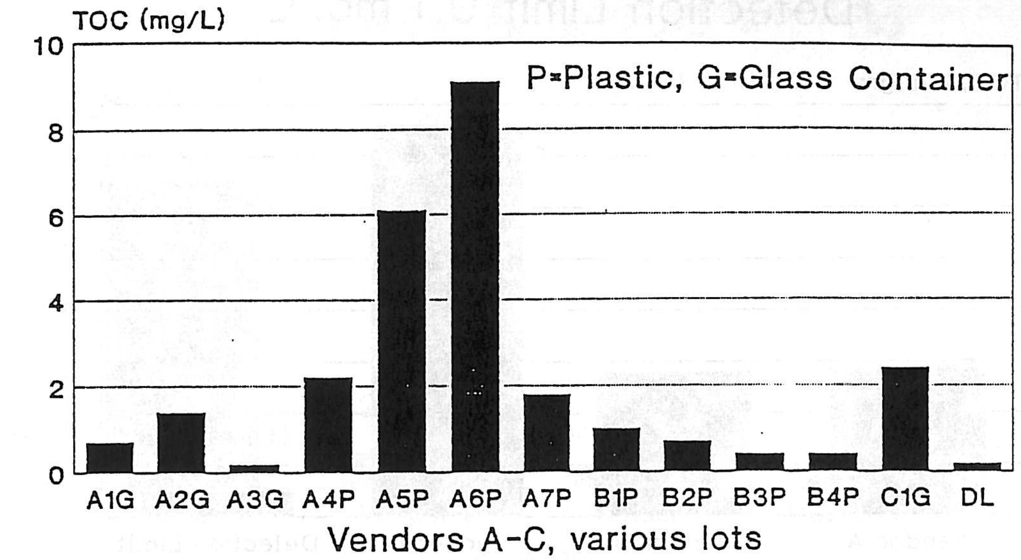
CONCLUSIONS

Organic compounds are commonly the highest level impurities in semiconductor processing fluids. Control of organic contaminant levels in chemicals may be crucial for production in the ULSI era. We feel it is essential that semiconductor processing chemical manufacturers begin monitoring and reducing the organic contaminant levels in their process chemicals. With the availability of the new analytical methods, TOC monitoring can now be routinely performed to see whether the TOC levels correlate with defects levels. TOC monitoring at the point-of-use may be useful when defining process bath lifetimes. On-site continuous reprocessing of chemicals is becoming more common since this can reduce waste, costs, and safety concerns, but possible TOC buildup must be monitored. When high TOC levels are observed, other techniques such as GC/MS or FTIR may be useful for the identification of the organic contaminants so that they may be eliminated at their source. Increased attention to TOC levels in chemicals may result in improvements in semiconductor yield and device performance. We look forward to working with chemical manufacturers and users to decrease the levels of organic impurities in semiconductor-grade chemicals.

FIGURE 1

TOC in Concentrated H2SO4

Typically 96-100% H2SO4



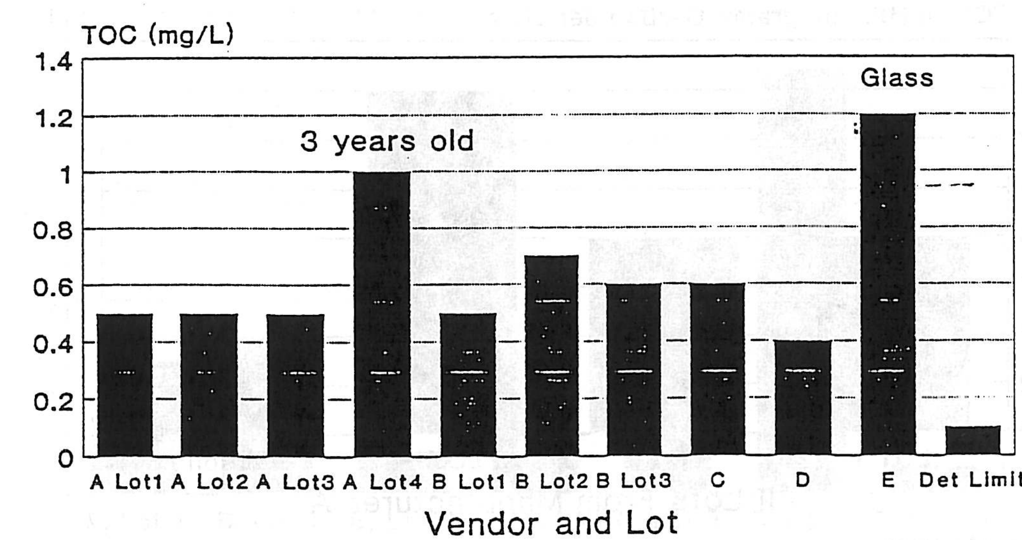
DL, Detection Limit, 0.2 mg/L
All SEMI-grade
A1G = Vendor A, lot 1, glass container

FIGURE 2

TOC in 85% Phosphoric Acid

All SEMI Grade

Detection limit, 0.1 mg/L

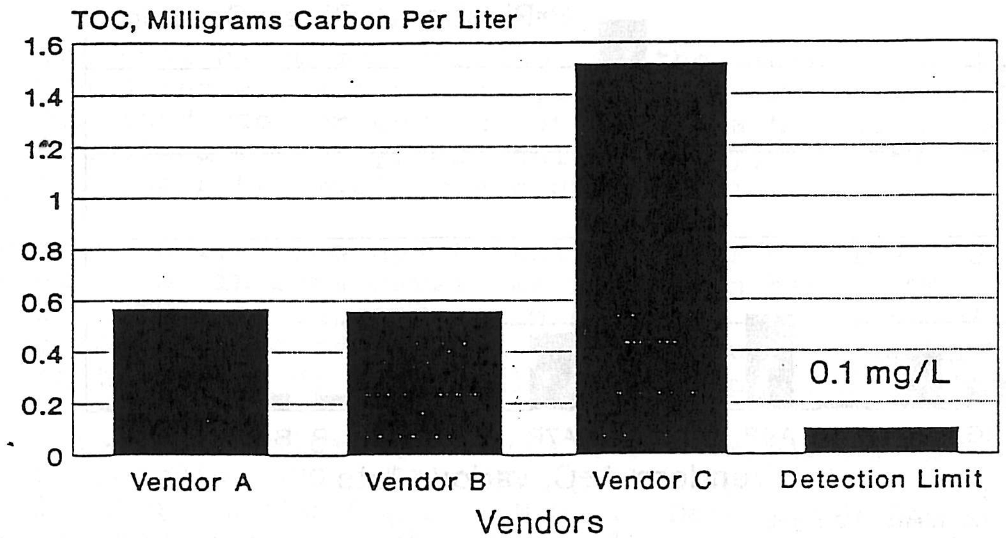


All in plastic jugs, except E in glass
Mfg A, Lot 4 expired, 3 years old

FIGURE 3

TOC in 49% SEMI-Grade HF

3 Vendors, HDPE Jugs
Detection Limit 0.1 mg/L

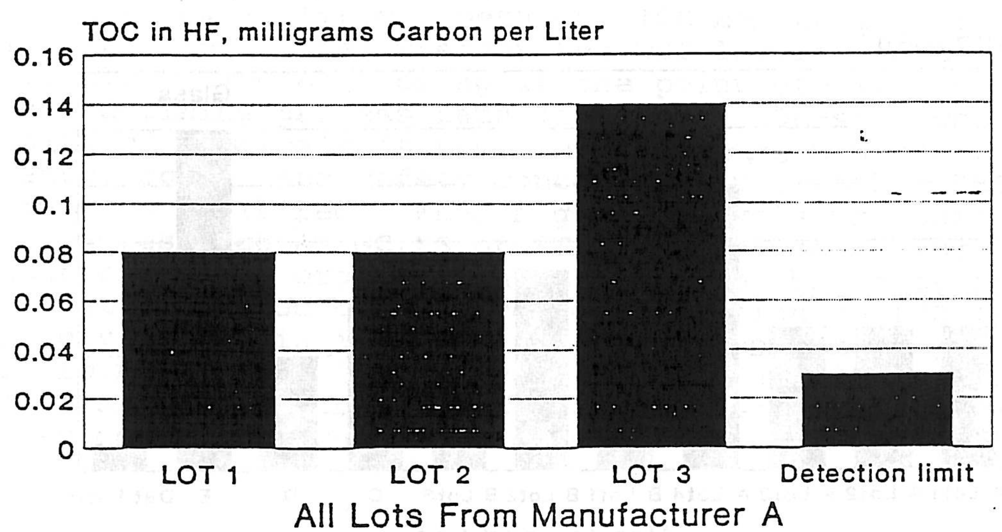


All samples 1-6 months old

FIGURE 4

TOC IN 10:1 SEMI GRADE HF

Detection limit 0.03 mg/L
Plastic jugs, all < 6 months old

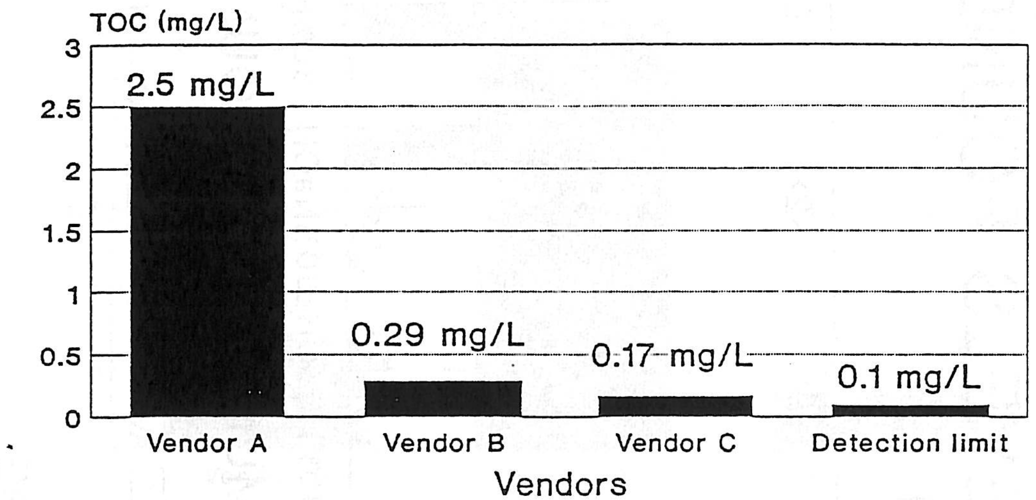


Single Manufacturer
Lot-to-Lot Variations
Approx 5% w/w HF

FIGURE 5

TOC in 40% w/w NH4F

3 manufacturers, plastic jugs
All bottles approx 2 years old

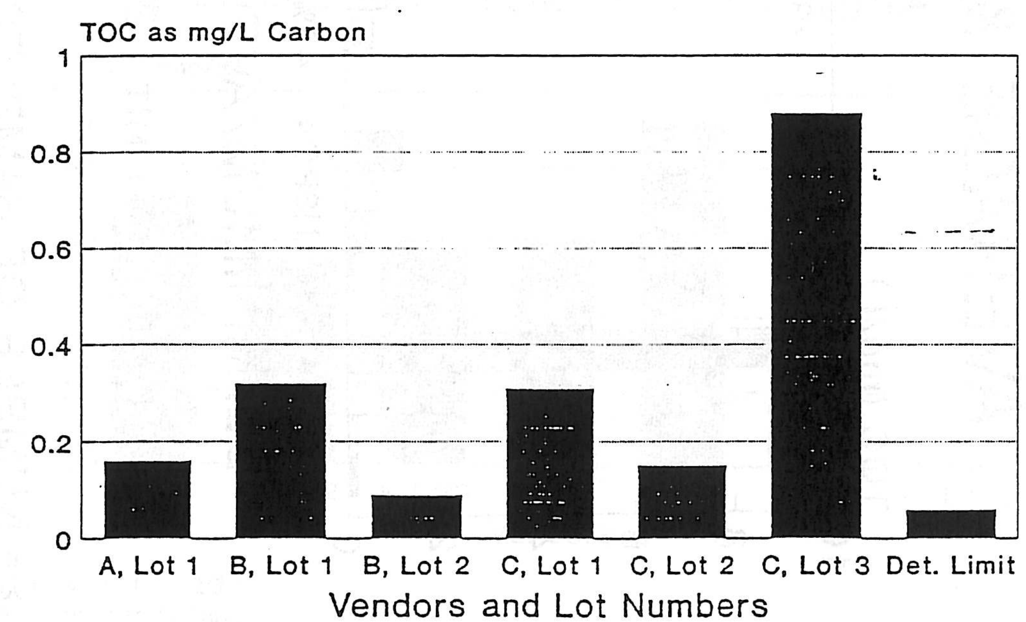


All SEMI-grade. 0.1mg/L Detection limit
Note that Vendor A bottle only is
discolored a tan color

FIGURE 6

TOC in NH4OH (28-30% NH3)

All SEMI grade, in plastic jugs

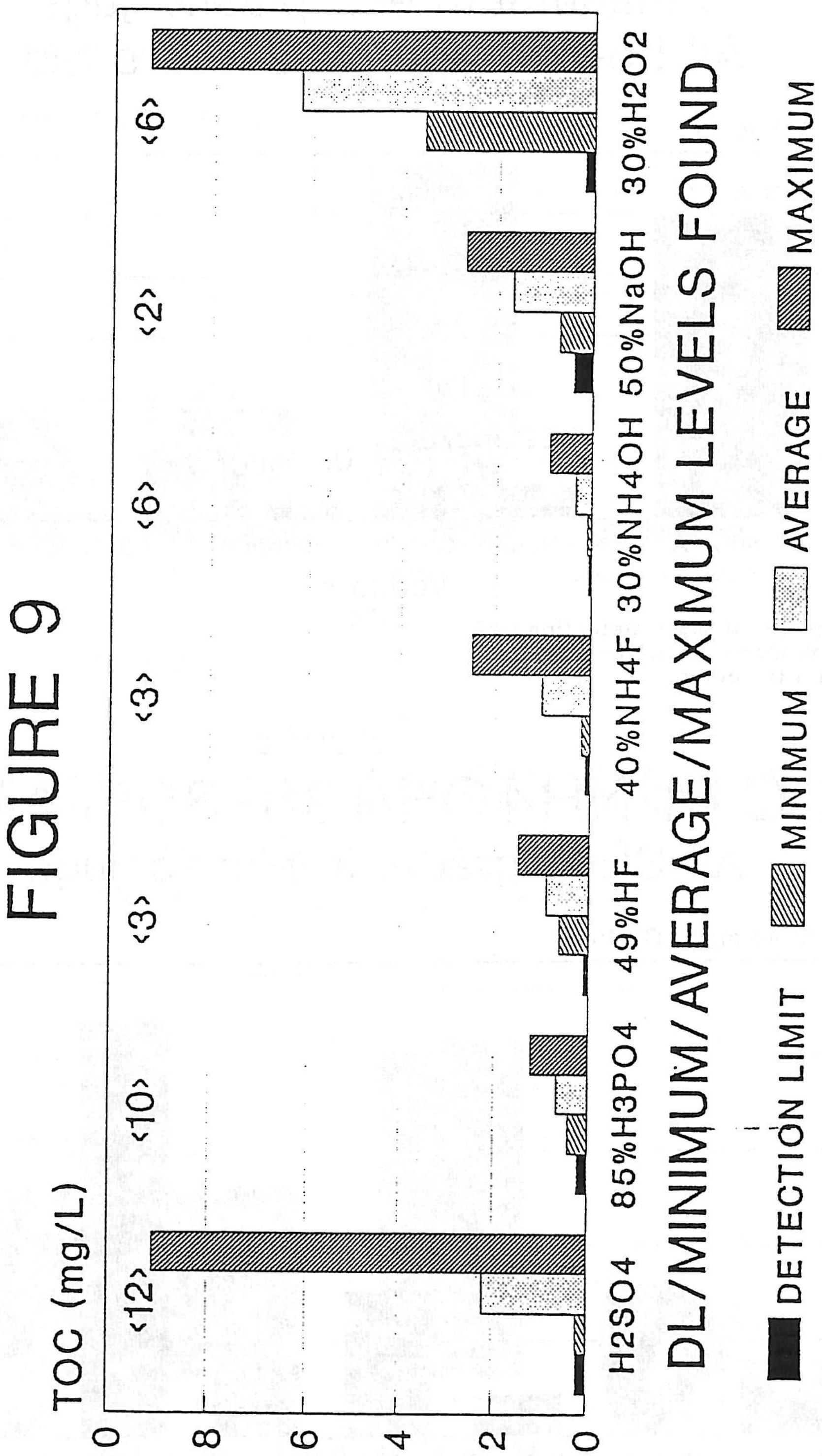


Estimated Detection Limit 0.06 mg/L

TOC IN CHEMICALS SUMMARY

DETECTION LIMITS & MINIMUM, AVERAGE & MAX LEVELS FOUND

FIGURE 9

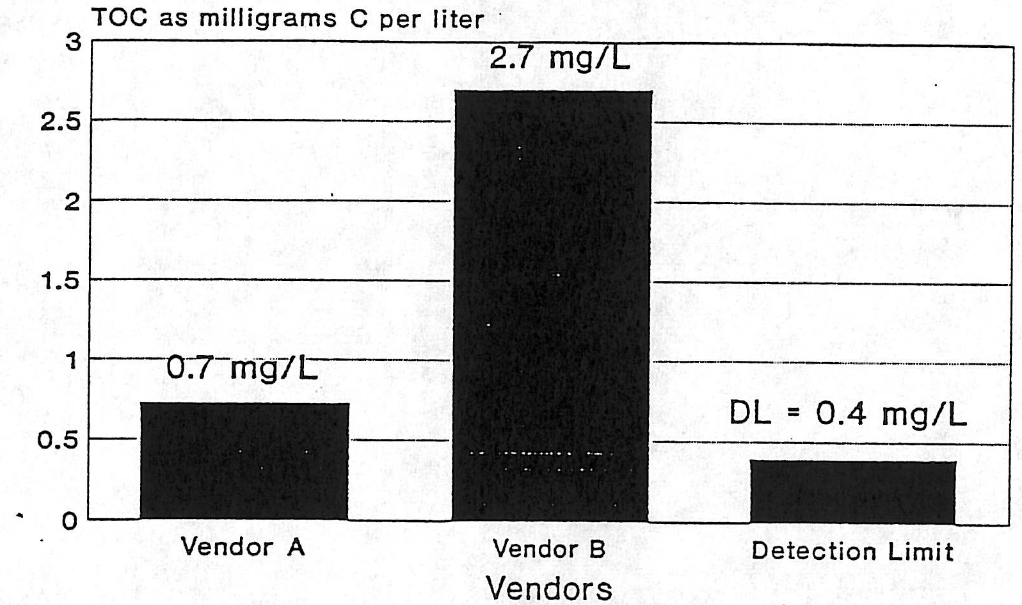


< > = NUMBER OF SAMPLES FOR AVERAGE

FIGURE 7

TOC in 50% NaOH

Reagent grades



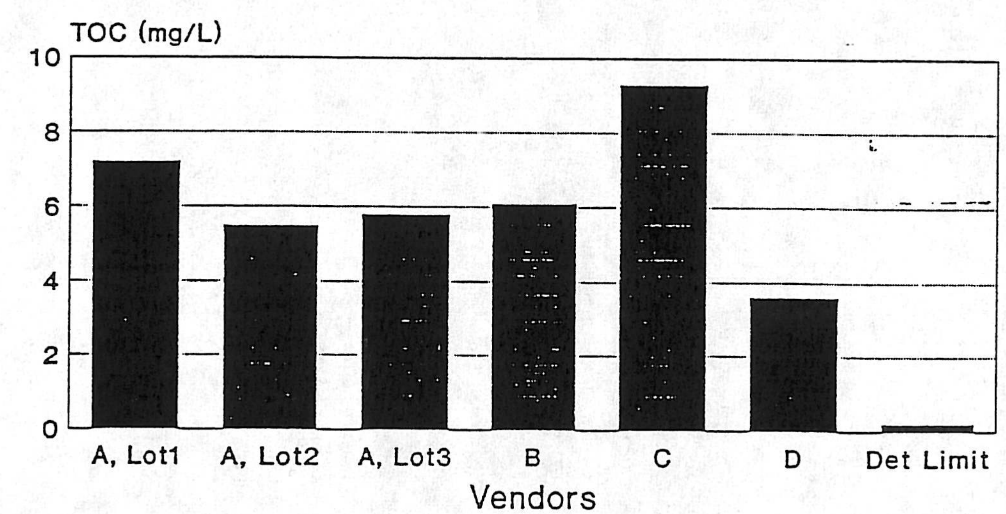
Detection Limit 0.4 mg/L

FIGURE 8

TOC in 30% Hydrogen Peroxide

Analyzed after decomposition using Pt

Estimated Detection Limit 0.2 mg/L



All SEMI grade

All from plastic jugs, typically HDPE