# Reactive Gas Sampling and Analysis for Metals

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## Abstract

A class of chemicals widely used in semiconductor processing is that of reactive, liquefied gases, such as dichlorosilane, trichlorosilane, anhydrous ammonia, and anhydrous HF. Delivery of these corrosive gases to the point-of-use, in a manner that avoids contamination by metallic elements, is an ongoing challenge. In addition, the metal impurity specifications for these chemicals are increasingly stringent. For example, in liquid-phase trichlorosilane iron is specified as low as 2 ppbw, and dopant impurities (B, As, P, Al) at 10 to 500 pptw.

This paper describes a sampling approach that has been applied to metal impurity analysis in a broad range of corrosive, liquefied gases. Results are presented for an on-site sampling campaign to qualify a newly installed trichlorosilane bulk supply system. In addition, the results are discussed in the context of wafer trace-metals analysis techniques, some of which represent indirect but highly sensitive methods for assessing trichlorosilane purity.

## Introduction

Reactive, liquefied gases, such as ammonia, hydrogen chloride, and hydrogen fluoride, as well as silicon-based specialty gases, such as silicon tetrafluoride and chlorosilanes, are widely used in semiconductor processing. These gases readily react with trace moisture, unintentionally introduced to the piping system in the course of cylinder changes or due to leaks, to yield corrosive byproducts (e.g. hydrochloric acid and ammonium hydroxide), which combine with stainless steel to contaminate the gas with metals. Thus a recurring problem in fabs is the contamination of reactive gases by stainless-steel related compounds, which may take the form of fine particles or volatile species (e.g. $FeCl_5$). Such contamination cannot be completely eliminated by filtration. When metal contaminants are detected on wafers, fabs lack the means

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to efficiently isolate the contamination source, and must resort to costly and time-consuming actions such as changing-out and testing the source cylinder, and/or replacing components or entire sections of the gas delivery system. Therefore we sought to develop a method for field sampling of corrosive gases to isolate or rule out potential contamination sources in a timely and cost-effective manner.

The objective of this work is a method for sampling TCS and other corrosive gases in the fab for off-site analysis of metal impurities. Anticipated sampling points are: 1) the gas jungle of the process tool, 2) the valve manifold box, and 3) the gas source (cabinet or tube trailer). Previously [1] we reported details of the lab-based method development stage. Here we report results for sampling liquid-phase trichlorosilane at a customer site.

## Sampling Approach

No technology has been established for direct analysis of the full range of trace metals in corrosive gases. Instead, trace metals quantification is accomplished in separate capture and analysis steps. The capture step usually takes one of three forms: hydrolysis, filtration, or residue. Hydrolysis entails chemical reaction of the reactive gas with an aqueous solution, to yield a homogenous, ambient vapor-pressure liquid that can be safely transported off-site for processing. Filtration involves passage of a known weight of the sample gas through a pre-cleaned membrane filter, which is subsequently leached and analyzed. In the residue method, a known weight of the reactive gas is liquefied or frozen in a cryogenically cooled vessel, and then slowly evaporated to leave behind non-volatile metals and particles. Hydrolysis was selected as the method of choice for field sampling of corrosive gases for two reasons: 1) anticipated high capture efficiencies for metals in any form, and 2) technical simplicity. An obvious weakness of the filtration and residue approaches is their inability to capture volatile metals, and (in the case of filtration) fine particles. Because hydrolysis involves intimate contact, indeed reaction, of the corrosive gas with water, high capture efficiencies were expected, and later confirmed by spike recovery tests.

## Reactive Gas Hydrolysis Chemistry

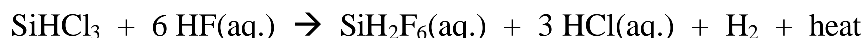
Some reactive gases (e.g. HF, HCl, and $NH_3$) are captured in water through a simple solvation process:

$NH_3 + H_2O(l) \rightarrow NH_3(aq.) + heat$

Other gases (e.g. chlorosilanes) are chemically transformed:

$SiHCl_3 + 3\,H_2O(l) \rightarrow HSi(OH)_3(aq.) + 3\,HCl(aq.) + heat$

In the case of silicon-based gases, addition of hydrofluoric acid converts silica to water-soluble fluorosilicic acid:



$SiHCl_3 + 6\,HF(aq.) \rightarrow SiH_2F_6(aq.) + 3\,HCl(aq.) + H_2 + heat$

The merits of the hydrolysis process can be summarized as follows:

1) transforms the reactive gas to a lower energy state with an ambient vapor pressure
2) yields a homogenous, aqueous solution that can be safely transported to the lab for matrix elimination and pre-concentration
3) captures all metallic contaminants regardless of their physical state (particle or volatile), due to intimate contact of the gas with the aqueous phase and chemical reaction

## Method Development

A method for hydrolysis sampling of reactive gases has been developed [1,2]. The sampling system consists of PTFE and PFA tubing and components to transfer the gas-phase or liquid-phase gas from a cylinder or piping system to an aqueous impinger, where hydrolysis takes place. The system regulates the flow of reactive gas to avoid violent boiling or over-heating of the impinger solution. Fig. 1 depicts how the system is implemented in the field.

### Spike Recovery Test

The potential for volatile metal analyte loss during TCS sample handling is well recognized [3-6], and the problem has led others to utilize complexing agents, such as mannitol, to stabilize volatile elements during the matrix elimination step. Because the use of adducting agents increases sample-handling complexity and cost, and because the metal content of supplemental reagents is variable and degrades detection limits for some elements, we do not use such

reagents. Instead, our sample-handling procedures are tailored to avoid loss of volatile metal compounds. Thus it was important to confirm that our sampling and sample-pretreatment methods provide satisfactory analyte recovery. A spike recovery test was carried out as follows. Four sample bottles were prepared, each containing 400g aqueous HF at the normal sampling concentration. Two of the bottles were spiked with 80 ng/element for the 34 elements in Table 1; the other two bottles were unspiked controls. Each of the four bottles was then used to sample around 45 g liquid-phase TCS following the procedure described previously. Table 1 displays recovery percentages calculated by the relation:

$$SR_A\ (\%) = 100\ \% * ( [A]_{spike} - [A]_{unspiked}) / 200\ \text{pptw}$$

where,

$SR_A$ (%) = percent spike recovery of element A

$[A]_{spike}$ = avg. concentration of A in spiked samples

$[A]_{unspiked}$ = avg. concentration of A in unspiked samples

200 pptw = parts-per-trillion-weight spike concentration

Our sampling and evaporation techniques yielded recoveries in the 83-115% range for all elements. Excellent recoveries were obtained for dopant elements (B, As, Sb, and Ge) as well as for stainless steel components (Fe, Cr, Ni, Mn, and Mo) that are typically included in TCS specifications. These data validate our sampling and pretreatment methods.

A separate spike recovery test had to be performed for phosphorous, as it is analyzed separately. Recovery was 100 +/- 10 % for a 1.0 ppbw spike, following the methodology outlined above.

## On-site Sampling of Trichlorosilane

TCS is a corrosive, liquefied gas widely used in the manufacture of semiconductor-grade silicon, and in the chemical vapor deposition (CVD) of epitaxial silicon. In these applications, TCS purity is essential since metallic and dopant impurities incorporated into silicon may alter device performance. In a fab, TCS is delivered to the tool either as a pressurized liquid, or

diluted in a carrier gas, such as hydrogen. TCS sampling is a particular challenge as it is a flammable, highly reactive, and corrosive gas.

A trichlorosilane sampling campaign was conducted at a customer site. The objective was to compare metal impurity concentrations in liquid-phase TCS originating from a newly installed and passivated TCS bulk supply system, with TCS from the traditional tote source. (A tote is a high-purity vessel about the size of a 55-gallon drum.) Fig. 1 depicts the sampling arrangement. Note that sampling was performed in a conventional gas cabinet and not in a cleanroom.

Sampling system installation, sample collection, and system decommissioning were completed in a single day. Analytical results were delivered 3 days later.

## Sample Pre-Treatment and Analysis

The 400-500 mL hydrolysis solution is slowly evaporated to near-dryness using a proprietary Air Liquide evaporation system specially designed to minimize metallic contamination during sample preparation. The sample is reconstituted with an aqueous solution of 2% $HNO_3$ [Fisher Optima grade] and 2% H2O2 [semiconductor grade] up to the original sample volume and analyzed by Dynamic Reaction Cell Inductively Coupled Plasma-Mass Spectrometry (DRC ICP-MS) (Perkin Elmer Elan 6000 DRC).

In Table 2, the method detection limit is calculated as the greater of 0.13 ppbw or the sample blank value. Note that although the DRC ICP-MS *instrument* detection limit is around 10 pptw for most elements, the effect of sample dilution and environmental contaminants leads to significantly higher *method* detection limits.

## TCS Metals Analysis Results

See Table 2. Six identical impinger bottles were utilized in the project. The shipping blank was transported to the site, but never opened. The sample blank was attached to the sampling system and purged with nitrogen to simulate all the steps of the sampling process. Finally, two samples of liquid-phase trichlorosilane were collected from the tote and bulk tank sources.

The cleanliness of the impingers and sampling system is demonstrated by the results of the shipping and sample blanks. In addition, sample-to-sample reproducibility was reasonable.

The elevated concentrations of iron, chrome, manganese, and nickel in the bulk TCS samples is believed due to incomplete passivation of the new bulk tank and piping system.

## Hydrolysis vs. Wafer Analysis Methods

A number of analytical tools are available for quantification of trace metals in silicon wafers [7]. Several of these methods offer an indirect means of assessing the purity of chlorosilane gases.

### TXRF

Total reflection X-ray fluorescence (TXRF) is used to quantify a range of *surface* metals on silicon films with a sensitivity of around 10E9 atoms/$cm^2$. Enhancements to conventional TXRF have been reported, for example utilizing vapor phase decomposition (VPD, see below) to concentrate the sample, or by combining VPD with synchrotron radiation as the light source, to achieve detection limits of around 10E7 atoms/$cm^2$ [7,8]. However, since the radiation reaches only to a depth of about 5 nm, the putative volume-based sensitivity is only 2E13 atoms/$cm^3$, or about 1 ppba (the density of pure silicon is 4.9E22 atoms/$cm^3$). Thus conventional TXRF, or even synchrotron-based TXRF methods, are unable to provide the sub-ppb sensitivity required for the technique to be useful for indirect analysis of metal impurities in chlorosilane gases.

### VPD-ICP-MS

Vapor phase decomposition inductively-coupled plasma mass spectroscopy (VPD-ICP-MS) is another technique employed to measure surface metals on wafers. Here the wafer is exposed to anhydrous HF vapor, which decomposes the surface oxide. Then a roughly 100 µL droplet of aqueous acid is swept over the surface to capture dissolved metals. This droplet is then typically diluted up to a volume of 1 mL before analysis by ICP-MS.

To compare the detection limits achievable by direct hydrolysis of e.g. dichlorosilane with VPD-IC-MS, we can simply compare the weights of silicon captured by each process and assume all subsequent sample treatment is the same. Our hydrolysis procedure typically captures 35 g dichlorosilane, corresponding to about 9.8 g silicon. On the other hand, the VPD sampling process normally etches the silicon film to a depth of less than 1 µm. For a 200 mm wafer, and assuming the entire wafer is scanned (about 284 $cm^2$, with a 5 mm edge exclusion), the weight of captured silicon is about 0.028 g. Thus, hydrolysis captures about 350x more sample than VPD-ICP-MS. Therefore, for the analysis of trace metals in cylinders, VPD-ICP-MS does not have any advantage over direct hydrolysis.

## NAA

In neutron activation analysis (NAA) the silicon sample is situated in a field of neutrons generated by a nuclear reactor. Trace impurity elements are converted to radioisotopes by neutron bombardment. The radioisotopes decay, and release gamma radiation at frequencies characteristic of the elements. NAA allows quantification of around 40 elements at sub-pptw to 10 ppbw detection limits.

In addition to limited availability, and lengthy analysis times for some elements, NAA cannot be used for light elements, such as boron, and is generally not useful for a number of key elements in silicon, including aluminum, magnesium, and phosphorous. Thus, NAA should be considered mainly as a highly sensitive technique that complements PL and/or LTFT-IR, outlined below.

## PL and LTFT-IR

The methods most often specified for quantification of metal impurities in trichlorosilane (and dichlorosilane) are photoluminescence (PL) spectroscopy or low-temperature Fourier-transform (LTFT-IR) spectroscopy of an epitaxial silicon layer deposited from the gas. ASTM standards for these methods were recently transferred to SEMI [9,10]. In both techniques, the sample is cooled to liquid He temperature, and exposed to radiation of an Ar ion laser (PL) or an infrared light source (LTFT-IR). The radiation stimulates light emissions at the characteristic frequencies of B, P, Al, and As in the silicon lattice. Detection limits for boron, phosphorous, arsenic, and aluminum with PL are around 2 ppta. For LTFT-IR, detection limits for B, P, As, Al, Sb, and Ga are on the order of 10 ppta.

These standards are concerned only with film analysis and not with the film deposition procedure. In addition, little is known about how impurities in the silicon-based reagent gas are incorporated into the film. Therefore PL and LTFT-IR should be viewed as highly sensitive but semi-quantitative tracking tools for source gas purity.

Detection limits for the hydrolysis based method hinge on 1) the extent to which the hydrolysis sample can be concentrated before analysis, and 2) background impurity concentrations, which cannot be overcome by sample concentration. For elements with background concentrations in our aqueous HF below 10 pptw, and assuming 10x sample dilution, 10x sample pre-concentration, and 10 pptw instrument detection limit for ICP-MS, method detection limits for hydrolysis below 10 pptw could be achieved. Currently our detection limits for boron and

phosphorous are limited to around 100 pptw and 1 ppbw, respectively, due to the concentrations of these elements in the impinger solutions.


## Summary

A hydrolysis-based sampling method was employed for field sampling of liquid-phase trichlorosilane, for off-site trace metals analysis. The method currently provides detection limits of around 100 pptw for most trace metals in chlorosilane gases. However, sample pre-concentration can potentially be exploited to reduce detection limits for many elements to below 10 pptw (calculated in the gas). While hydrolysis combined with ICP-MS can compete with indirect techniques, such as NAA, PL, and LTFT-IR in terms of sensitivity, for some elements (especially boron and phosphorous) the method detection limit is significantly higher due to high blank concentrations.

## Bios

Dan Cowles

Dan Cowles, Ph.D. has been with Air Liquide for 10 years, including 3 years in Air Liquide's Tsukuba, Japan R&D Center. His work has focused on reactive gas sampling and analysis, process tool exhaust characterization, and analysis of trace organics in liquid chemicals. Currently he is working on a variety of applied R&D projects in Air Liquide's Dallas Chemical Center.

Cowles received a Ph.D. degree in Physical Chemistry from the University of Colorado-Boulder, Boulder, CO, and a B.A. degree in Chemistry from the University of Oregon, Eugene, OR.

David Bollinger

David Bollinger is a research chemist at Air Liquide-Balaz Analytical Services located in Dallas, Texas. David holds a B.S. degree in Biochemistry from the University of North Texas, and has worked as a research chemist in the semiconductor area for twelve years. He has authored and co-authored numerous papers and presentations on semiconductor process chemical analyses and contamination studies. David is also currently attending the University of Texas at Dallas working towards a doctoral degree in Chemistry.

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[8] J. Wang, M.K. Balazs, P. Pianetta, K. Baur, and S. Brennan, SPWCC, 2001.

[9] ASTM Standards F 1389-00 and F 1630-00

[10] SEMI Standards MF 1389-00 and MF 1630-00

| Element | SR (%) | Element | SR (%) |
|---|---|---|---|
| Li | 92 | Ga | 94 |
| Be | 94 | Ge | 88 |
| B | 94 | As | 95 |
| Na | 91 | Sr | 90 |
| Mg | 93 | Zr | 90 |
| Al | 91 | Nb | 96 |
| K | 92 | Mo | 83 |
| Ca | 85 | Ag | 85 |
| Ti | 93 | Cd | 93 |
| V | 92 | In | 90 |
| Cr | 89 | Sn | 89 |
| Mn | 93 | Sb | 89 |
| Fe | 112 | Ba | 89 |
| Co | 97 | Ta | 88 |
| Ni | 115 | Tl | 89 |
| Cu | 97 | Pb | 91 |
| Zn | 97 | Bi | 88 |

Table 1. Spike Recovery Results.

| Element | Shipping Blank | Sample Blank | Tote TCS 1 | Tote TCS 2 | Bulk Tank TCS 1 | Bulk Tank TCS 2 |
|---|---|---|---|---|---|---|
| **Li** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Be** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **B** | <0.13 | <0.13 | 0.26 | 0.33 | 0.66 | 0.66 |
| **Na** | <0.13 | <0.13 | <0.13 | 0.20 | 0.26 | 0.26 |
| **Mg** | <0.13 | <0.13 | <0.13 | <0.13 | 0.26 | 0.26 |
| **Al** | <0.13 | <0.13 | <0.13 | 0.59 | 0.52 | 0.53 |
| **K** | <0.13 | 0.13 | <0.13 | <0.13 | 0.26 | <0.13 |
| **Ca** | 0.26 | 0.26 | 2.6 | 13.7 | 3.5 | 2.1 |
| **Ti** | <0.13 | <0.13 | <0.13 | 0.40 | 0.26 | <0.13 |
| **V** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Cr** | <0.13 | <0.13 | 1.6 | 2.0 | 2.2 | 2.5 |
| **Mn** | <0.13 | <0.13 | <0.13 | <0.13 | 0.39 | 0.40 |
| **Fe** | 0.13 | 0.13 | 9.7 | 14.9 | 33.2 | 23.6 |
| **Co** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Ni** | <0.13 | <0.13 | 0.64 | 0.73 | 0.92 | 1.06 |
| **Cu** | <0.13 | <0.13 | <0.13 | 0.13 | 0.13 | 0.26 |
| **Zn** | <0.13 | <0.13 | <0.13 | <0.13 | 0.26 | 0.26 |
| **Ga** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Ge** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **As** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Sr** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Zr** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Nb** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Mo** | <0.13 | <0.13 | 1.73 | 0.99 | 1.31 | 1.58 |
| **Pd** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Ag** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Cd** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **In** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Sn** | <0.13 | <0.13 | <0.13 | <0.13 | 0.39 | 0.53 |
| **Sb** | <0.13 | <0.13 | <0.13 | <0.13 | 0.52 | 0.79 |
| **Ba** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **La** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Ta** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **W** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Pt** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Au** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Tl** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Pb** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| **Bi** | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |

Table 2. On-site TCS Sampling Results (unit = ppbw)

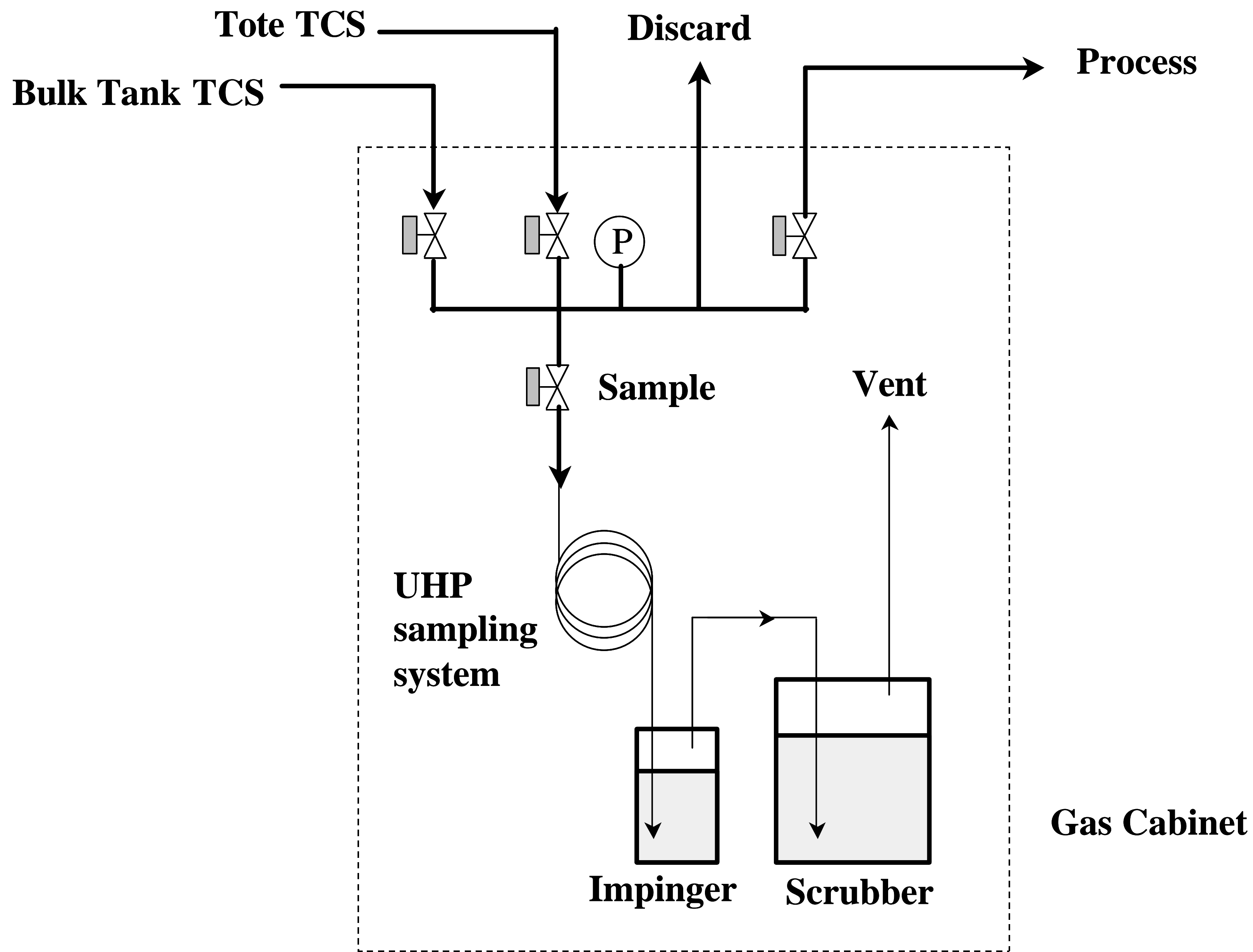




Fig. 1. Apparatus for field sampling of liquid-phase trichlorosilane.