



Project Summary

Laboratory and Field Evaluations of a Methodology for Determining Hexavalent Chromium Emissions from Stationary Sources

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Development of methodology for sampling and analysis of chromium to support stationary source regulations was initiated in 1984. This study was initiated to determine whether chromium emissions should be regulated under Section 112 of the Clean Air Act National Emissions Standards for Hazardous Air Pollutants (NESHAP). To support stationary source regulations, it is important that (1) the sampling procedure not change the chromium valence state during sampling and (2) an analytical technique for measuring low concentration levels of chromium be available. These goals are achieved with the current EPA "Draft Method for Sampling and Analysis of Hexavalent Chromium at Stationary Sources."

The draft method utilizes a recirculating system to flush impinger reagent into the sampling nozzle during sample collection. Immediate contact of the stack gas with impinger reagent "fixes" the chromium valence state.

Ion chromatography coupled with a post column reaction system and an ultraviolet visible detector is used to analyze Cr(VI) in the parts per trillion range.

Field tests were conducted at metal plating facilities, industrial cooling towers, municipal waste incinerators, sewage sludge incinerators, and hazardous waste incinerators. It was at the hazardous waste facility that the new method was proven to have acceptable precision and essentially no conversion in the sample train. Stan-

dard deviations for the sampling runs were determined.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Sampling and Analytical Procedures

A "dry" test method was developed for collection of Cr(VI) with intended application at stationary sources with filterable, dry emissions. This method involved collection of particulate emissions by use of Method 5 (Appendix B, 40 CFR Part 60). Under Method 5, stack gas is isokinetically drawn through a sampling probe and glass fiber filter. Colorimetric analysis using a spectrophotometer with an optimum wavelength of 540 nm was used to detect the specific wavelength generated by diphenylcarbazide when complexed with Cr(VI) in the filter digest. Tests employing this method were conducted at a ferrochrome smelter, a chemical plant, and a refractory brick plant.

Testing of the Method 5 sampling train continued in various studies at coal fired boilers, municipal waste combustors and chrome plating facilities. It was determined that this method was unable to effectively collect chromium from these sources, thus an impinger technique (Method 13-type train) was developed to collect the mist or droplets containing soluble chromium.



Twelve paired test runs were performed at a chromium plating facility to compare the two test methods.

The impinger train consisted of a stainless steel nozzle, a heated glass lined probe, filter bypass, two reagent impingers containing 0.1 N sodium hydroxide (NaOH), an empty impinger, filter, and silica gel impinger. Further studies and data comparisons allowed the elimination of the filter. The train was operated isokinetically using Method 5 sampling procedures. Sample was recovered using a deionized water rinse. Analysis for Cr(VI) was the same as that described for the Method 5 sampling technique. The impinger method sampling train corrected some of the problems associated with chromium determinations at facilities with effluent streams containing mist or aerosols. Documented results from chrome plating facilities indicated that the method was acceptable. Questions remained, however, concerning Cr(VI) conversion.

Further field studies of the stationary sources with potential Cr(VI) emissions included a series of cooling towers. It was at cooling tower facilities that the need for a low level analytical technique for measurement of hexavalent chromium was critical. Methods of reducing sample volume for better detectability with the colorimetric method proved to be unacceptable. Also, reducing sample volume increases the chances of chemically altering the valence form of the collected chromium before Cr(VI) determinations have been achieved.

A second series of cooling tower test incorporated the following changes to the sampling technique: (1) the collection media was changed from deionized water to 0.1 N NaOH, and (2) an additional rinse of the sampling train with nitric acid was added to the recovery process. These rinses were included to determine how much chromium remained in the impingers after the first rinse, and to loosen any insoluble chromium from the walls of the impingers.

A very important aspect of this series of cooling tower tests was the realization that chromium is converting somewhere between the tower and the sampling train. Efforts to determine where the conversion was occurring and to identify an analytical technique with acceptable detection limits were undertaken in a series of laboratory and field tests.

The analytical technique selected for evaluation was ion chromatography (IC) coupled with a Cr(VI)-specific post column reaction. The Cr(VI)-specific post column reaction employs the diphenylcarbazide chromophor identical to the colorimetric

procedures used in the earlier tests. IC however provides much greater sensitivity. A preconcentration technique extends the sensitivity of this system to the parts per trillion range. This IC procedure allows separation of Cr(VI) in the basic collection media, eliminating potential biases from sample preparation.

The development of this analytical technique revolutionized the development of a stationary source test method for measurement of Cr(VI). It was now possible to directly measure Cr(VI) at levels as low as 100 parts per trillion.

The development of a sampling train which would prevent the conversion of Cr(VI) was necessary to obtain representative measurements of stack gas. Because laboratory studies showed that the potential exist for conversion of Cr(VI) to Cr(III) in the glass-lined probe of the Method 13-type train, a sampling device which eliminated the "dry" probe surface area was designed. Employing this design allows immediate contact of the Cr(VI) with the basic impinger reagent as the stack gas enters the sampling train. This immediate contact allows the reagent to dissolve the chromium and stabilize the Cr(VI) in the gas stream. The recirculating reagent also provides continuous rinsing of the sample line. To minimize background contamination often noted with the glass components of the impinger train, the new recirculating (RC) train was constructed of Teflon. Conventional glass impingers were used for the nitric acid and silica gel impingers. A schematic of this recirculating sample train is presented in Figure 1.

Following the development of the RC sampling train, laboratory studies were conducted to select the most suitable collection reagent. Several series of laboratory and field studies were conducted. To trace the chromium during the experimental procedures, a radioactively labeled chromium isotope, ($^{51}\text{Cr(VI)}$) was employed. This radioisotope has a half-life of 27.7 days, which provides ample analysis time yet relatively fast disposal. The isotope is also available with high specific activity (high radioactivity) from a minute concentration of Cr(VI) which is not detectable by the ion chromatographic technique.

Employing this radioisotope, the first series of laboratory studies was conducted and based on the results of the study, isopropyl alcohol/sodium hydroxide (IPA/NaOH) solution was selected for field evaluation.

Following field tests of the IPA/NaOH reagent and analytical difficulties associated with analyzing the samples collected

in this reagent, a second series of test were conducted to evaluate other reagents. In this series of test, the NaOH reagent was found to be acceptable for preventing conversion of Cr(VI).

A third laboratory experiment was conducted when it was discovered that the effects of dissolved gases, which can bring about the reduction of Cr(VI), could be removed by purging the sample train with nitrogen following the test run.

The newly design RC sampling train does not include a filter. Particulate matter is collected in the impinger portion of the sampling train during sample collection. The presence of this particulate matter can generate a positive or negative bias in Cr(VI) determinations. Because of the potential conversion an immediate post-run filtration was conducted.

Finally, field evaluations to compare the new RC sampling train with the previous impinger train were conducted. Two field tests were performed at a cooling tower facility. In both tests, the RC train and the Method 13-type train were operated simultaneously.

During the initial field test, four collocated trains (two RC and two Method 13-type) were operated at two separate locations. This test was conducted to compare the conversion percentages for each type of train.

The second field test was designed to determine the extent of conversion of Cr(VI) to Cr(III) in the RC train. The radioactive tracer, $^{51}\text{Cr(VI)}$, was added to the impinger reagent prior to sampling. The isotope would be exposed to the same conditions as the native Cr(VI) collected from the cooling tower. If any $^{51}\text{Cr(VI)}$ converted to Cr(III) during sampling then the train would most likely be responsible for the conversion.

In conjunction with efforts to develop procedures for sampling and analysis of chromium and nickel species from sewage sludge incinerators, another field study was conducted. Two types of sewage sludge incinerators were visited, a multiple-hearth facility and a fluidized bed facility. Chromium determinations were difficult at these facilities due to the high organic content of the effluent stream.

The final study was an emissions field test performed at a hazardous waste incinerator. The facility included a rotary kiln, secondary combustion chamber, electrostatic precipitator and packed column scrubber. The procedures followed were those of the current "Draft Method for Determination of Cr(VI) at Stationary Sources."

For developmental purposes, the impinger reagent was again spiked with

the radioisotope $^{51}\text{Cr(VI)}$. The radioisotope data was used to determine recovery efficiency of the method and the amount of conversion that occurred in the sampling train.

Results and Discussion

The original hexavalent chromium method was limited to stationary sources with filterable dry emissions. Also, the limit of detection for the colorimetric technique was determined to be 0.1 ppmv, but the concentration of the samples had to be above 10 ppmv due to a series of dilutions required during sample preparation. When the test method was evaluated at the three facilities mentioned earlier, it was assumed that trivalent and hexavalent chromium were collected on the filter and in the probe rinse in the same ratio as emitted from the stack. Later testing revealed that collection procedures can cause changes in the valence state of the chromium compound.

To compare the new Method 13-type sampling procedures with the Method 5 sampling procedures 12 paired test runs were performed at two separate locations of a chrome plating facility. The data indicated that the dry filter method resulted in values 10 to 25 percent lower than the Cr(VI) values obtained from the impinger trains. At this time, the Method 5-type sampling procedures for collecting chromium were deemed unacceptable.

The Method 13 evaluations at chromium plating facilities indicated that, in almost all cases, the amount of Cr(VI) collected appeared to be over 80 percent of the total catch. Trivalent chromium however, was determined as the difference between total chromium and Cr(VI). Based on these results the Method 13-type sampling techniques were acceptable for the determination of chromium. This type of sampling train corrected some of the problems associated with chromium determinations at facilities with effluent streams containing mist or aerosols. The question of chromium conversion remained.

The first set of Method 13-type data obtained at a cooling tower resulted in highly variable data. The restrictions of the analytical detection limits coupled with the use of deionized water as the collection media rather than a basic solution may have contributed to the variable results. Possible conversion in the sampling train during sampling may have also added to biased results.

At the facility hosting the second series of cooling tower tests, as much as 90 percent of the chromium collected was trivalent. The chromium in the recirculating

cooling water at the facility was typically 99 percent Cr(VI). These data lead to the conclusion that conversion of Cr(VI) to Cr(III) was occurring in the cooling tower, in the Method 13-type sampling train, or in both. This conversion phenomenon and the inability to directly analyze for Cr(VI) in low concentration levels were possibly the key factors in the Cr(VI) method development studies.

Finally, an analytical method was identified for direct low-level Cr(VI) analyses. The limit of detection for measurement of Cr(VI) using an ion chromatographic post column reaction (IC/PCR) system was determined to be 0.16 parts per billion (ppb), with a quantifiable limit of 0.5 ppb. When preconcentration was employed, the limit of detection was lowered to 0.05 ppb. The upper range of detection without dilution of the samples was determined to be 1 ppm.

The IC/PCR was linear over two orders of magnitude. Precision, in terms of relative standard deviation, was 5.2 percent based on analysis of 10 samples. Accuracy, determined by analysis of a suitably diluted EPA audit sample averaged 6.7 percent for 7 analyses over a one month period. With the addition of an *in situ* preconcentration technique it was determined that up to 30 mL of a 0.5 ppb standard solution could be loaded on the preconcentration column before significant breakthrough occurred. With the injection of a 20 mL sample, the sensitivity of the technique was increased over 60-fold, yielding a limit of quantification of less than 100 ppt. Accuracy at this level, in terms of percent error, was determined to be ± 9.5 percent.

Laboratory studies conducted to select the most suitable collection reagent yielded data which indicated that an IPA/NaOH solution would be the most effective collection media. However, the anion exchange column used in sample analysis was not designed for use with organic compounds and the capacity of the column was decreased over the course of the sample analyses. Also, the IPA was evaporating at extremely rapid rates during field sampling, thus resulting in loss of impinger solution before the end of the sample run.

In the second series of tests, NaOH was found to be acceptable. In two separate test runs, recovery of Cr(VI) was above 97 percent.

The third laboratory test conducted included the use of a posttest nitrogen purge. Sodium hydroxide and sodium bicarbonate reagents had favorable results with over 90 percent Cr(VI) recovery. As shown in Table 1, these data indicate that the

trains purged with nitrogen have a higher final pH than those not purged. The purge helps to reduce dissolved gases in the collected sample which may lead to oxidation of the Cr(VI) ion.

Results from the initial field test of the new RC train (compared with the Method 13-type train) indicated that conversion was still occurring in either the cooling tower or the sample trains. The RC train, however, did show an average conversion 20 percent less than that of the Method 13-type train.

The data collected from the second field evaluation of the RC train revealed Cr(VI) to Cr(III) conversions of 71 percent for the RC train and 81 percent for the Method 13-type train. The probe of the Method 13-type train was recovered separately and revealed conversions of 88 percent. (Conversion of Cr(VI) to Cr(III) was determined by ratios of Cr(VI) to total chromium.) Following the cooling tower tests, all further studies were conducted only using the RC sampling system.

Results of testing conducted at the sewage sludge incinerator indicated that this method may not be acceptable at facilities with high organic content. Conversion of the chromium was as high as 45 percent at one of the facilities. Analysis of inlet sample was impossible due to loss of column capacity.

The final field study, at a hazardous waste incinerator, was the first field test to indicate essentially no sample bias from the sampling procedures. The radioactive data indicated that 100 percent of the radioactive spike was accounted for when all components of the train were collected. The impinger solution however, only accounted for 75 percent of the total.

Analysis of the filter digestion solutions and IC eluant indicated that only 1 percent of the Cr(VI) spiked into the train was reduced during sampling.

Hexavalent chromium and total chromium determinations were made for each sampling train, and means and standard deviations were calculated for each run. The results are shown in Table 2.

The variance of the Cr(VI) measurements were tested using the Bartlett test and was found to be homogeneous throughout the entire six runs. Therefore, it was possible to calculate standard deviations from the combined variances that were more representative of the data than the standard deviation of any run. Thus, the standard deviations of the Cr(VI) measurements for Runs 1 - 3 and 4 - 6 were 0.9 and 9.5 $\mu\text{g/dscm}$, respectively. The value for the total chromium measurements was 27 $\mu\text{g/dscm}$.

Table 1. Media Collection Experiment Using Nitrogen Purge

Solution	Initial	Posttest (without purge)	Posttest (with purge)
Ammonium acetate			
pH Level	7	5.5	6.00
Average (%) Conversion	-	-22.12	-10.49
Sodium Bicarbonate			
pH Level	9	8.0	9.00
Average (%) Conversion	-	6.59	1.00
Sodium hydroxide			
pH Level	13	8.0	9.00
Average (%) Conversion	-	16.71	9.70
Sodium acetate			
pH Level	7	5.5	6.00
Average (%) Conversion	-	100	100

Test results from this field evaluation indicated that the RC train performed adequately. The collection efficiency of the impingers was improved from 75 percent to 95+ percent with the addition of a fourth deionized water rinse.

Conclusions and Recommendations

The major goals of the methods development program were (1) to develop the sampling procedures that do not change the oxidation state of chromium during sampling and (2) to identify a readily available analytical technique for measuring low-concentration levels of Cr(VI). These goals have been achieved.

Many years of challenging work have resulted in a draft test method for chromium that does not affect the valence state of the compound as it enters the sample train, and the identification of an analytical technique with the ability to analyze concentrations of Cr(VI) in the ppt range.

Several major discoveries were made during the development of the draft method:

It was determined that conversion of Cr(VI) to Cr(III) was occurring in the

sample collection system. Until this sample collection bias was eliminated, no accurate data could be obtained.

When an investigation of a surrogate compound for chromium was evaluated, it was discovered that emissions ratios and cooling tower water ratios were not the same. This assumption had been applied to chromium for several earlier cooling tower tests. Calculating a value for Cr(VI) was no longer possible based on these assumptions. A direct analysis technique was necessary.

Poor precision between sampling trains during the test evaluations generated questions about the recovery process. It had been assumed that the collected chromium was water soluble. In truth, the variability between sampling runs was caused in part by the poor recovery of insoluble chromium. An acid rinse was added to remove the insoluble chromium from the glassware.

A recirculating sample train was developed to "rinse" the sample probe

continuously during sample collection. This design allowed immediate contact of the stack gas with the impinger reagents.

A low-level analytical technique for analyzing Cr(VI) was utilized. Ion chromatography with a post column reaction (IC/PCR) allowed detection of Cr(VI) in the ppt range. The availability of this technique increased the variety of sources to which the sampling method could be applied.

The use of a radioactive tracer greatly increased knowledge of the behavior of chromium in the sampling train. For the first time, the chromium could be "followed" through the collection procedure. Use of the tracer ultimately allowed accurate determination of conversion caused by sampling.

A study of the effects of sulfur dioxide (SO₂) on Cr(VI) was conducted. This study generated information which (1) led to better choices of collection media and (2) emphasized the need to remove SO₂ from the collected sample.

A nitrogen purge following sample collection was added to the method. The nitrogen purge removed dissolved gases that may react with chromium. The solutions were then recovered and filtered, which removed insoluble Cr(III) compounds that may be slowly oxidized.

Many of the discoveries mentioned above may have invalidated data that had been collected prior to correction of the sampling or analytical problems. Thus except for data obtained using the draft method, any data should be regarded with caution.

Further studies to optimize and confirm the validity of this method should be conducted:

Because the analytical technique (IC/PCR) of this draft method is not commonly available to most laboratories, alternative techniques would be desirable. It is possible that a preconcentration technique, coupled with colorimetric spectrophotometric analysis, could be an alternative to IC/PCR, although no studies have been conducted to date.

Comparisons of a glass recirculating sample train with the Teflon RC train should be conducted. Some data has been generated to indicate that glass components are not acceptable when

Table 2. Measurement of Cr(VI) from Hazardous Waste Incinerator

Condition 1. Aqueous Cr+3 fed into process.

Condition 2. Aqueous Cr+6 fed into process.

Run	Sample Train	Isokinetic Sampling		Total Cr+6 ($\mu\text{g/dscm}$)	Total Chromium ($\mu\text{g/dscm}$)	Cr+6/ Total Chromium	Run	Sample Train	Isokinetic Sampling		Total Cr+6 ($\mu\text{g/dscm}$)	Total Chromium ($\mu\text{g/dscm}$)	Cr+6/ Total Chromium
		Rate (%)	Moisture Content (%)						Rate (%)	Moisture Content (%)			
1	A	97.9	19.2	0.357	116.259	0.3%	4	A	105.7	21.8	89.828	114.150	78.7%
	B	100.3	21.8	0.415	187.124	0.2%		B	102.8	22.5	107.569	132.319	81.3%
	C	95.4	21.7	0.367	153.084	0.2%		C	99.2	23.3	106.129	126.789	83.7%
	D	100.1	21.9	0.179	110.081	0.2%		D	103.6	23.4	120.440	127.646	94.4%
	Average RSD		21.2	6.1%	0.330	141.637		24.7%	Average RSD		22.8	3.5%	105.991
2	A	No results					5	A	104.6	24.1	76.618	117.440	65.2%
	B	No results						B	106.0	25.4	76.666	00.136	76.6%
	C	98.8	23.0	0.305	138.288	0.2%		C	102.6	24.4	74.534	160.521	46.4%
	D	98.2	21.7	0.355	87.611	0.4%		D	103.8	23.7	76.729	99.606	77.0%
	Average RSD		22.4	3.4%	0.330	112.950		35.5%	Average RSD		24.4	3.0%	76.137
3	A	99.7	23.2	0.410	42.196	1.0%	6	A	102.8	20.6	43.426	56.117	77.4%
	B	95.2	23.3	0.440	47.199	0.9%		B	91.1	24.7	57.280	129.892	44.1%
	C	93.3	22.7	0.575	48.737	1.2%		C	95.0	24.0	50.419	59.788	84.3%
	D	No results						D	92.5	24.1	52.977	72.414	73.2%
	Average RSD		23.1	1.4%	0.475	46.044		11.4%	Average RSD		23.4	8.0%	51.025

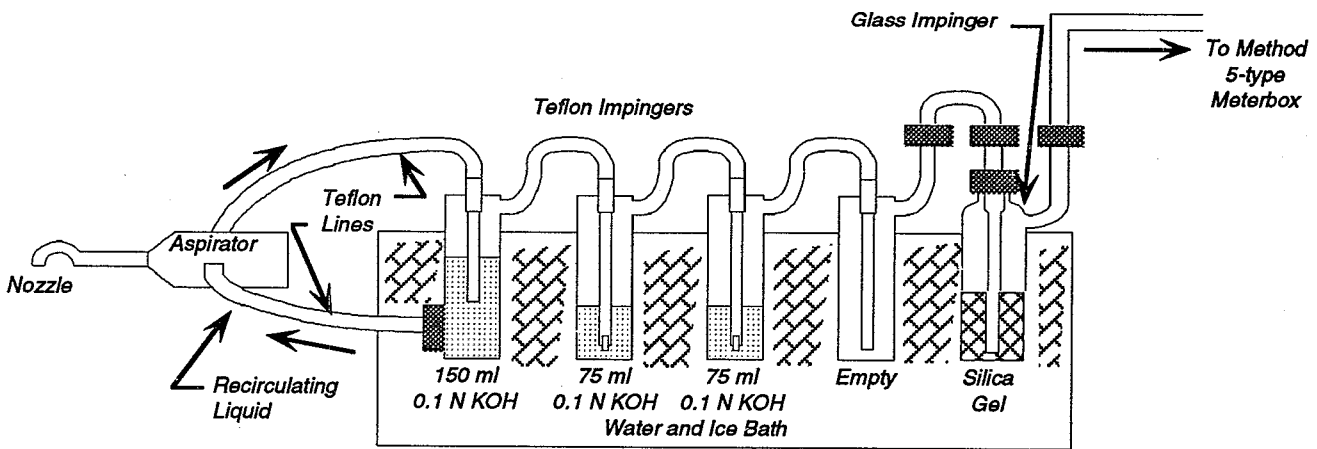


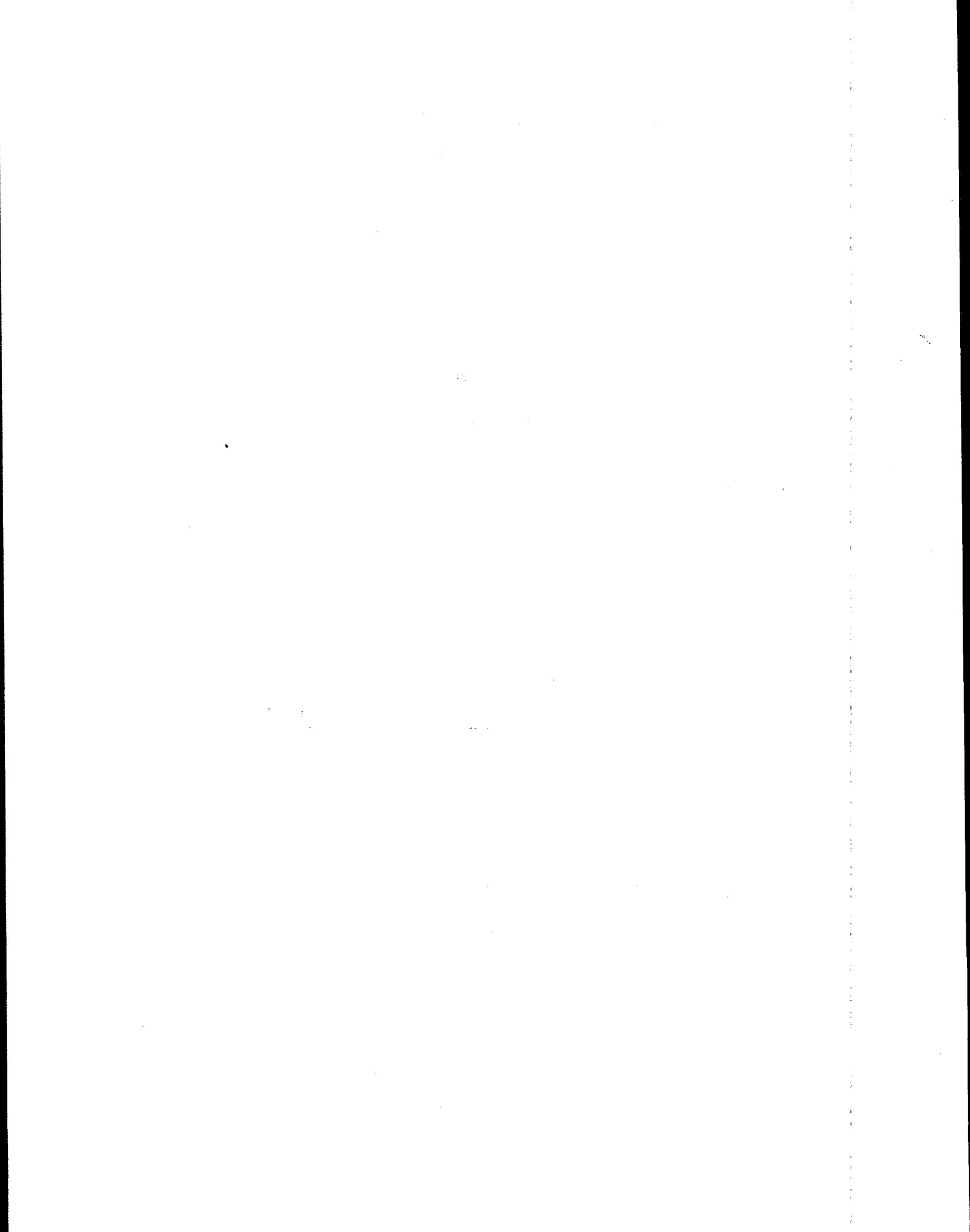
Figure 1. Schematic of recirculating sampling system.

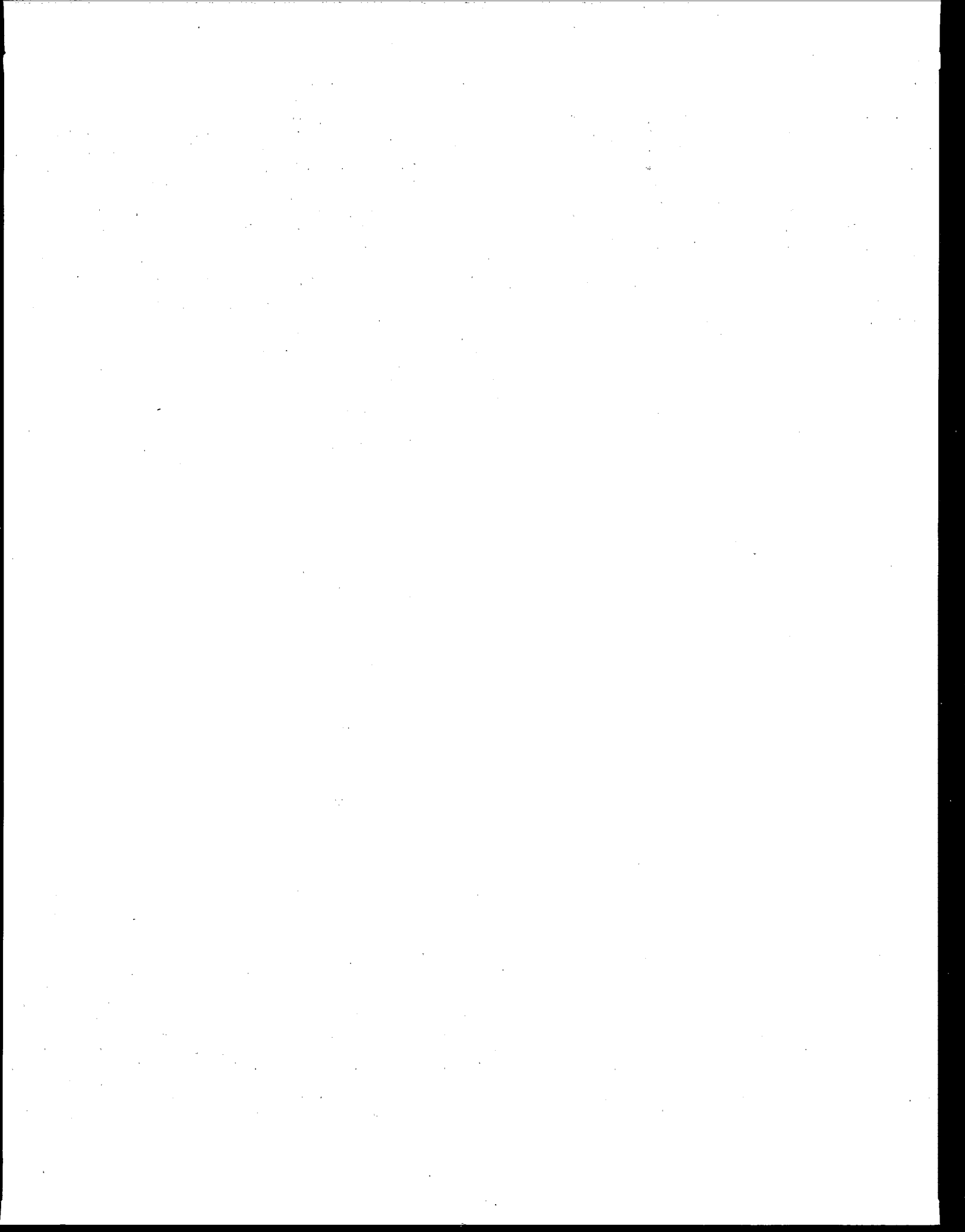
quantifying Cr(VI); however, glass coupled with recirculation has not yet been investigated.

Laboratory studies should be conducted to document that C-flex tub-

ing does not cause oxidation of Cr(VI). Because this material is not inert, it is possible that off-gassing during heating releases compounds that could convert the chromium.

And evaluations are needed if the draft method is to be applied at locations with temperatures above 400°F and with high SO₂ concentrations.





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*The complete report, entitled "Laboratory and Field Evaluations of a Methodology for
Determining Hexavalent Chromium Emissions from Stationary Sources," (Order No. PB92-
101336AS; Cost: \$26.00 (subject to change) will be available only from:*

*National Technical Information Service
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