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Evaluation of SO_4 data compatibility and
approaches for salvaging historical data.

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**EVALUATION OF SO₄ DATA
COMPATIBILITY AND APPROACHES FOR
SALVAGING HISTORICAL DATA**

by

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MANAGEMENT PERSPECTIVE

In the study of acid rain, there has been a great deal of discussion and concern over the analysis of sulfate particularly in coloured waters. This study was carried out at the request of WQB, Headquarters, to investigate the validity of colorimetric and ion chromatography methods for determining SO_4 in coloured water. The study provides concrete evidence that ion chromatography results on organic-contaminated coloured waters are reliable and the colorimetric data are biased high. An approach for salvaging historical colorimetric data was found.

ABSTRACT

The compatibility and reliability of colorimetric and chromatographic SO_4 data were evaluated. The multiple standard addition technique was applied to numerous natural and humic acid fortified waters. A total of more than 20 different waters was used, in which the colour ranged from 50 to 440 H.U. and the organic carbon from 0.7 to 20 ppm. For the first time, it was demonstrated that Ion Chromatography (IC) data on organic-contaminated coloured waters are reliable. It was also confirmed that the Methyl Thymol Blue (MTB) colorimetric data were biased high. An approach for salvaging historical colorimetric data was found and briefly discussed.

INTRODUCTION

There has been a great deal of discussion and concern over the analysis of sulfate in coloured waters. This is due to its importance in the study of acid rain, and to its questionable colorimetric data caused by interference from coloured matter in the waters.

Early sulfate data were generated by the colorimetric method using methyl thymol blue (MTB). The validity of these data have been discussed in several papers (1-7). Many scientists believe that these data are biased high (4-7).

The high bias of MTB results was suspected as early as 1979 by Cronan (8). In 1980, Crowther (9) also reported high MTB results in comparison to ion chromatography (IC) results for water samples from Dorset area. The report suggested that the colorimetric method was invalid due to the presence of tannins, lignins, humates and fulvates whereas the IC methodology was relatively unaffected by these interferences. In 1981, Cheam (10) conducted an interlaboratory special quality control study on soft and coloured waters and observed significant difference between MTB and IC results.

Although the IC methodology appears to be unaffected by colour interferences, the reliability of sulfate data generated by IC has not been established (11). Uncertain data lead to uncertain

interpretations and conclusions. If sound conclusions are to be made, the reliability of analytical data must be first ensured. Thus in this paper, we wish to evaluate in detail the compatibility of MTB and IC data and to establish their reliability (or non-reliability). A brief discussion on handling historical data will also be made.

STUDY DESIGN

Establishing data compatibility or reliability would be greatly simplified if pertinent certified reference materials (CRMs) are available. Since there are no coloured water CRMs, the study design is more complicated and time consuming.

The design utilizes the principle of multiple standard additions (12-16) and many different types of organic-contaminated waters, including seven different natural coloured waters from the Atlantic and Ontario regions (Table 1) and many humic acid fortified coloured waters (Table 2). In addition to establishing data compatibility and reliability, the design generates pertinent data for evaluating the approaches to salvage historical data.

By studying the commercial humic acid (H.A.) along with natural organic matter in coloured waters, we diversified the types of organic matter studied, and at the same time were able to create a more even spread of colours.

EXPERIMENTAL

Multiple standard addition (MSA)

An advantage of MSA is its ability to diagnose the amount present in an unknown. Bader (15) pointed out that in nearly every case, an appropriate method of standard addition can give the best absolute value for an unknown. In our case, the MSA experimental design is schematically presented in Figure 1 where sample $\text{SO}_4\text{-N}$ represents each of the principal natural samples (Table 1) and humic acid fortified samples (Table 2).

Before subjecting the samples to MSA, the original approximate SO_4 concentrations, x_0 , of the natural waters (Table 1) were determined. For H.A. fortified samples $\text{SO}_4\text{-X}$ to $\text{SO}_4\text{-XIV}$ (Table 2), the original SO_4 concentrations were found to be very small; subsequently, each was spiked with 2 ppm SO_4 to produce samples $\text{SO}_4\text{-XIV}$ to $\text{SO}_4\text{-XVII}$, and with 5 ppm SO_4 to produce samples $\text{SO}_4\text{-XXII}$ to $\text{SO}_4\text{-XXV}$ (Table 2). These spiked values were taken as original approximate concentrations, x_0 , of the fortified samples.

Each of the samples was then subsampled into four groups of triplicate subsamples according to the scheme in Fig. 1, and to each subsample was added a known SO_4 stock volume to yield a final added concentration equal to $0.0 x_0$; $0.5 x_0$, $1 x_0$ and $2 x_0$. (Note

that a stock solution of 1000 ppm SO_4 was used so that only a very small volume was added. This resulted in a negligible dilution effect). Each of these subsamples was further subdivided into duplicate subsamples for the various analyses shown in Figure 1. Effectively, there are six replicate analyses of each group of subsamples with a known added SO_4 level.

The original spikes of 2 and 5 ppm SO_4 (Table 2) were chosen because six out of seven natural samples used (Table 1) had concentrations within this range. The colour 250 H.U. of fortified waters (Table 2) was studied to provide a more evenly spaced colour range than natural waters. Also the pH was adjusted to approximately 4.3 so that it is within the usual acid rain pH of 4-5. To avoid precipitation (17), only -1 ppm Ba was added to two samples, SO_4 -XXX and SO_4 -XXXI, to see whether there is any Ba interference or problem associated with its presence.

Analyses

The ion chromatography analyses of SO_4 were carried out using an automated Dionex 2100 system. All samples were filtered before being introduced into a 50 μL sample loop. The eluent was prepared by dissolving 2.25 g of Na_2CO_3 and 2.25 g of NaHCO_3 in 10L of deionized distilled water. The eluent flow rate was 2.0 mL/minute. The sample passed through a guard column or precolumn, a separator

column, an anion fibre suppressor with dilute H_2SO_4 as regenerant, and finally a conductivity detector. The detected signal was amplified and converted to concentration through a Hewlett Packard recorder/integrator.

The colorimetric SO_4 measurements were carried out using the automated methylthymol blue (MTB) method, coded as NAQUADAT No. 16306 (18). Using equimolar solution of BaCl_2 and MTB, the method allows Ba to react with SO_4 at low pH; then at high pH, Ba reacts with MTB, leaving a grey uncomplexed MTB, which is measured and equated to SO_4 concentration present in the sample.

Dissolved organic carbon (DOC in ppm) was analysed by the IR Analyser Method, Naquadat code 06101 (18); pH was measured using a Radiometer PHM64 meter. Apparent colour, in Hazen Units, was determined by visual comparison using a Hellige Aqua Tester. Specific conductance was measured using a CDM-83 conductivity meter, and Ba by the Atomic Absorption direct aspiration technique, Naquadat code 56101 (18).

Chemicals, Glass and Plasticware

Humic acid was purchased from Aldrich Chemical Co. Inc. (Lot No. HD061197); Na_2SO_4 , Na_2CO_3 and NaHCO_3 from J.T. Baker Chemical Company. All containers were cleaned with Chromerge and stored in

distilled water for at least one week before use (19). Stocks and standards were made in volumetric flasks, whereas the test samples were in plastic containers with sizes ranging from 50 mL to 500 mL.

RESULTS AND DISCUSSION

Compatibility and reliability of MTB and IC data

The applicability of the MSA requires that the recoveries be uniform, the addition line be straight and parallel to standard line, the dilution effect be minimal, and the addition of standard be about 0.5, 1.0 and 2.0 times the original values in the samples (Figure 1). In total, we applied the MSA procedure to 15 different samples - seven natural coloured waters (Table 1) and eight humic acid fortified coloured waters (Table 2). Each of these 15 water samples was analyzed by IC and MTB methods before and after multiple standard additions.

The general behaviour of MSA application to the MTB and IC methods of these 15 water samples are illustrated in Figure 2. The ordinate represents the analytical response or the amount found by direct analysis, whereas the abscissa represents the concentration added and the amount "present" by extrapolation of addition line. The amount present is defined as the absolute abscissa value at the

intersection of the abscissa line and the extrapolated least-squared addition line.

The MTB line (Figure 2) is curved, which indicates existence of interference and hence uncertainty of data. This curvature makes extrapolation meaningless. But if the line was extrapolated, the amount "present" would be higher than the amount found, which is unacceptable. Table 3 summarizes the two types of amounts and indeed indicates that the amount present is in general higher than the amount found. Table 3 further shows that the results for samples SO_4 -XIV to SO_4 -XVII increase with colour and DOC, and are much higher than the expected 2 ppm; likewise, the results for sample SO_4 -XXII to SO_4 -XXV increase with colour and DOC and are higher than the expected 5 ppm. Thus, the MTB results are not reliable. Finally, the MTB results are higher than, ^{and} thus not compatible with, the IC results (Table 3 vs. Tables 4, 5 and 6).

The IC standard and addition lines representing each of the 15 samples are depicted in Figure 3 to Figure 17, respectively. For natural waters, Figures 3-9 present the MSA plots of IC analyses. In every case, except for SO_4 -III, the criteria of uniformity and parallelism as dictated by the MSA are obeyed. For SO_4 -III, we observed slight downward curvature at the third addition ($=2 x_0$), which corresponds to a high SO_4 level of nearly 30 ppm. To avoid this concentration effect, we diluted the solutions two times, obtained a

straight addition line (Figure 4) and then calculated the amounts as with the other samples.

Table 4 compares the SO_4 amounts obtained by direct analysis (amount found) and by MSA (amount present) for the natural waters, and shows good agreement within experimental errors. This gave assurance that IC produces reliable results in presence of organic matter in natural waters.

For humic acid fortified waters, at colour 50, 90, 225 and 440 H.U., the addition lines also indicate uniformity and parallelism (Figures 10-13). In these four samples, the original spike was 2 ppm, so the "true" SO_4 value can be taken as 2 ppm since the background concentrations were very small (Table 5, SO_4 -X to SO_4 -XIII). Table 5 also shows good agreement between the two SO_4 amounts determined by direct analysis and by MSA. These amounts represent for all practical purposes 100% of the true value, that is amount found = amount present = true amount, indicating data reliability.

For higher SO_4 levels in four other humic acid fortified waters, Figures 14-17 and Table 6 clearly indicate excellent agreement between the three amounts, found-present-true, thus adding further substantiation that the data obtained by IC are unaffected by interferences from colour and various types of organic matter, and are therefore reliable.

Other Possible Interferents

Crowther (9) tested possible interference from pH, Fe(II), Mn(VII), humic acid, tannic acid and lignin sulfate on a single standard addition of 10 ppm SO_4 and found that the IC recoveries were satisfactory.

The presence of barium may cause chemical interference. Before the introduction of Ba to samples to be tested, we estimated the amount of Ba which could be added without precipitation of BaSO_4 , using the solubility product data (17). One ppm was estimated to be safe and this amount was added to two HA fortified waters having colour of 50 and 440 H.U. and 2 ppm SO_4 . The recoveries of SO_4 as determined by IC were ~100% (Table 5, SO_4 -XXX, SO_4 -XXXI). These results indicate that Ba, also, causes no interference and hence further substantiates the reliability of IC data.

Approaches for Salvaging Historical Data

Having established the quality of data generated by the IC and MTB methods, we proceeded to explore and evaluate ~~the~~ approaches ~~in order~~ to salvage historical MTB colorimetric data. This evaluation is lengthy and will be communicated elsewhere. The following briefly summarizes the findings:

- 1) There is no simple and universal correction factor which readily converts the historical data to true SO_4 values.
- 2) However, we have found that for a specific amount and nature of organic matter, there exists a relationship between SO_4 determined by MTB and SO_4 determined by IC. Thus, to salvage historical MTB data, we simply obtain case by case the two types of SO_4 values, relate them by a polynomial equation, and interpolate the corresponding historical values to obtain the expected true SO_4 values. The case by case treatment can involve a specific site, river, lake, or a group of them which have similar amount and nature of organic matter.

CONCLUSIONS

Using more than 20 different organic-contaminated waters, with a colour range of 50-440 H.U. and a dissolved organic carbon range of 0.7-20 ppm, we have demonstrated for the first time that the ion chromatography method gives reliable results. The ion chromatography data and the MTB colorimetric data are not compatible, the latter being consistently biased high.

We also found an approach for salvaging historical colorimetric data based on observed relationship between SO_4 by colorimetry and SO_4 by ion chromatography for each specified case. The relationship makes the correction of historical data possible by simple interpolation.

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TABLE 1. IDENTIFICATION OF NATURAL SAMPLES

Sample Name	Origin	Colour
SO ₄ -I	Pebbleloggitch, Atlantic Region	100
SO ₄ -III	Moose River, Ontario Region	60
SO ₄ -IV	Dickie Lake, Ontario Region (Dorset area)	100
SO ₄ -V	Atkins Brook, Atlantic Region	160
SO ₄ -VI	Upper Mercy River, Atlantic Region	90
SO ₄ -VII	Mount Tom Brook, Atlantic Region	100
SO ₄ -VIII	Sand Pond Atlantic Region	400

TABLE 2. HUMIC ACID (HA) FORTIFIED COLOURED WATERS

(All values are rounded design values)

Sample Name	SO ₄ Original Spike, ppm	Colour H.U.	H.A. Spike mg/L	pH Adjusted	Ba Spike ppm
SO ₄ -X	0	60	6	4.3	0
SO ₄ -XI	0	100	10	4.3	0
SO ₄ -XII	0	250	25	4.3	0
SO ₄ -XIII	0	400	40	4.3	0
SO ₄ -XIV	2	60	6	4.3	0
SO ₄ -XV	2	100	10	4.3	0
SO ₄ -XVI	2	250	25	4.3	0
SO ₄ -XVII	2	400	40	4.3	0
SO ₄ -XXII	5	60	6	4.3	0
SO ₄ -XXIII	5	100	10	4.3	0
SO ₄ -XXIV	5	250	25	4.3	0
SO ₄ -XXV	5	400	40	4.3	0
SO ₄ -XXX	2	60	6	4.3	1
SO ₄ -XXXI	2	400	40	4.3	1

TABLE 3. COMPARISON OF C_{MTB} RESULTS OBTAINED BY DIRECT ANALYSIS AND BY MSA IN NATURAL AND FORTIFIED SAMPLES*

Sample	Direct Analysis (amount found)	MSA (amount present)
SO ₄ -I	5.50 ± 0.52	6.64 ± 2.26
SO ₄ -III	9.60 ± 0.20	9.21 ± 0.15
SO ₄ -IV	4.73 ± 0.06	10.20 ± 4.94
SO ₄ -V	6.13 ± 0.83	10.52 ± 2.52
SO ₄ -VI	6.44 ± 0.48	6.80 ± 0.87
SO ₄ -VII	5.17 ± 0.31	7.47 ± 1.74
SO ₄ -VIII	9.57 ± 0.12	8.18 ± 0.10
SO ₄ -XIV	3.07 ± 0.17	3.54 ± 0.40
SO ₄ -XV	3.50 ± 0.12	4.11 ± 0.27
SO ₄ -XVI	5.82 ± 0.12	6.40 ± 0.45
SO ₄ -XVII	8.40 ± 0.13	10.95 ± 0.66
SO ₄ -XXII	6.75 ± 0.16	7.42 ± 0.48
SO ₄ -XXIII	5.38 ± 0.08	5.17 ± 0.32
SO ₄ -XXIV	7.63 ± 0.23	7.42 ± 0.62
SO ₄ -XXV	10.74 ± 0.06	12.14 ± 1.40

* C_{MTB} = SO₄ concentration by MTB method.

TABLE 4. COMPARISON OF C_{IC} RESULTS OBTAINED
BY DIRECT ANALYSIS AND BY MSA IN NATURAL WATERS*

Sample	Direct Analysis (amount found)	MSA (amount present)
SO ₄ -I	2.86 ± 0.18	2.37 ± 0.16
SO ₄ -III	8.99 ± 0.32	8.95 ± 0.45
SO ₄ -IV	1.61 ± 0.11	1.63 ± 0.19
SO ₄ -V	1.67 ± 0.08	1.56 ± 0.31
SO ₄ -VI	5.10 ± 0.12	4.96 ± 0.15
SO ₄ -VII	2.08 ± 0.15	1.93 ± 0.36
SO ₄ -VIII	1.95 ± 0.06	2.39 ± 0.42

* C_{IC} = SO₄ concentration by IC method.

TABLE 5. COMPARISON OF C_{IC} RESULTS OBTAINED BY
DIRECT ANALYSIS AND BY MSA IN HUMIC ACID FORTIFIED SAMPLES*
(AT 2 PPM SO_4 SPIKE LEVEL)

Sample	Direct Analysis	MSA
	(Amount Found)	(Amount Present)
SO_4 -X	0.06 \pm 0.03	
SO_4 -XI	0.06 \pm 0.02	
SO_4 -XII	0.08 \pm 0.02	
SO_4 -XIII	0.11 \pm 0.02	
SO_4 -XIV	2.17 \pm 0.15	2.19 \pm 0.19
SO_4 -XV	2.09 \pm 0.07	2.03 \pm 0.05
SO_4 -XVI	2.20 \pm 0.19	2.09 \pm 0.18
SO_4 -XVII	2.07 \pm 0.02	2.05 \pm 0.05
SO_4 -XXX	2.07 \pm 0.03	
SO_4 -XXXI	2.18 \pm 0.03	

* C_{IC} = SO_4 concentration by IC method.

TABLE 6. COMPARISON OF C_{IC} RESULTS OBTAINED BY
DIRECT ANALYSIS AND BY MSA IN HUMIC ACID FORTIFIED SAMPLES*
(AT 5 PPM SO_4 SPIKE LEVEL)

Sample	Direct Analysis (Amount Found)	MSA (Amount Present)
SO_4 -XXII	5.68 ± 0.08	5.54 ± 0.15
SO_4 -XXIII	5.09 ± 0.07	5.03 ± 0.02
SO_4 -XXIV	5.16 ± 0.03	5.05 ± 0.10
SO_4 -XXV	5.09 ± 0.06	5.06 ± 0.17

* C_{IC} = SO_4 concentration by IC method.

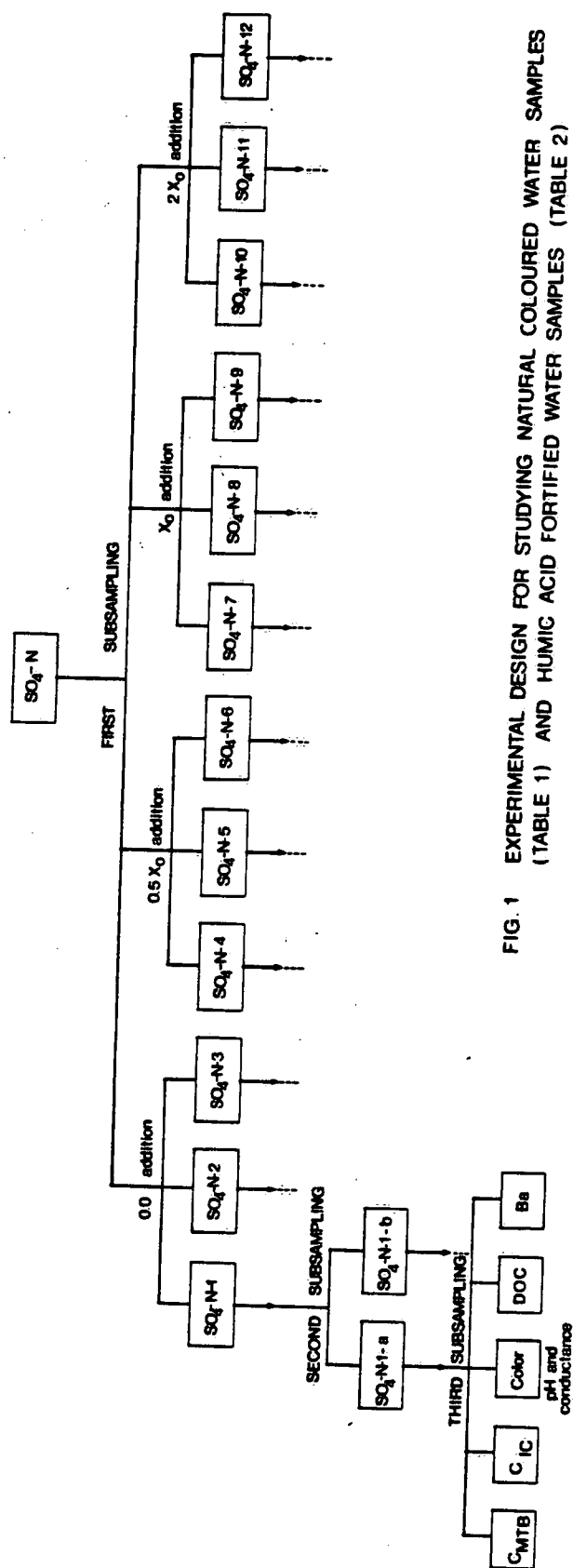


FIG. 1 EXPERIMENTAL DESIGN FOR STUDYING NATURAL COLOURED WATER SAMPLES (TABLE 1) AND HUMIC ACID FORTIFIED WATER SAMPLES (TABLE 2)

C_{MTB} = SO_4 concentration by MTB method
 C_{IC} = SO_4 concentration by IC method
 DOC = dissolved organic carbon

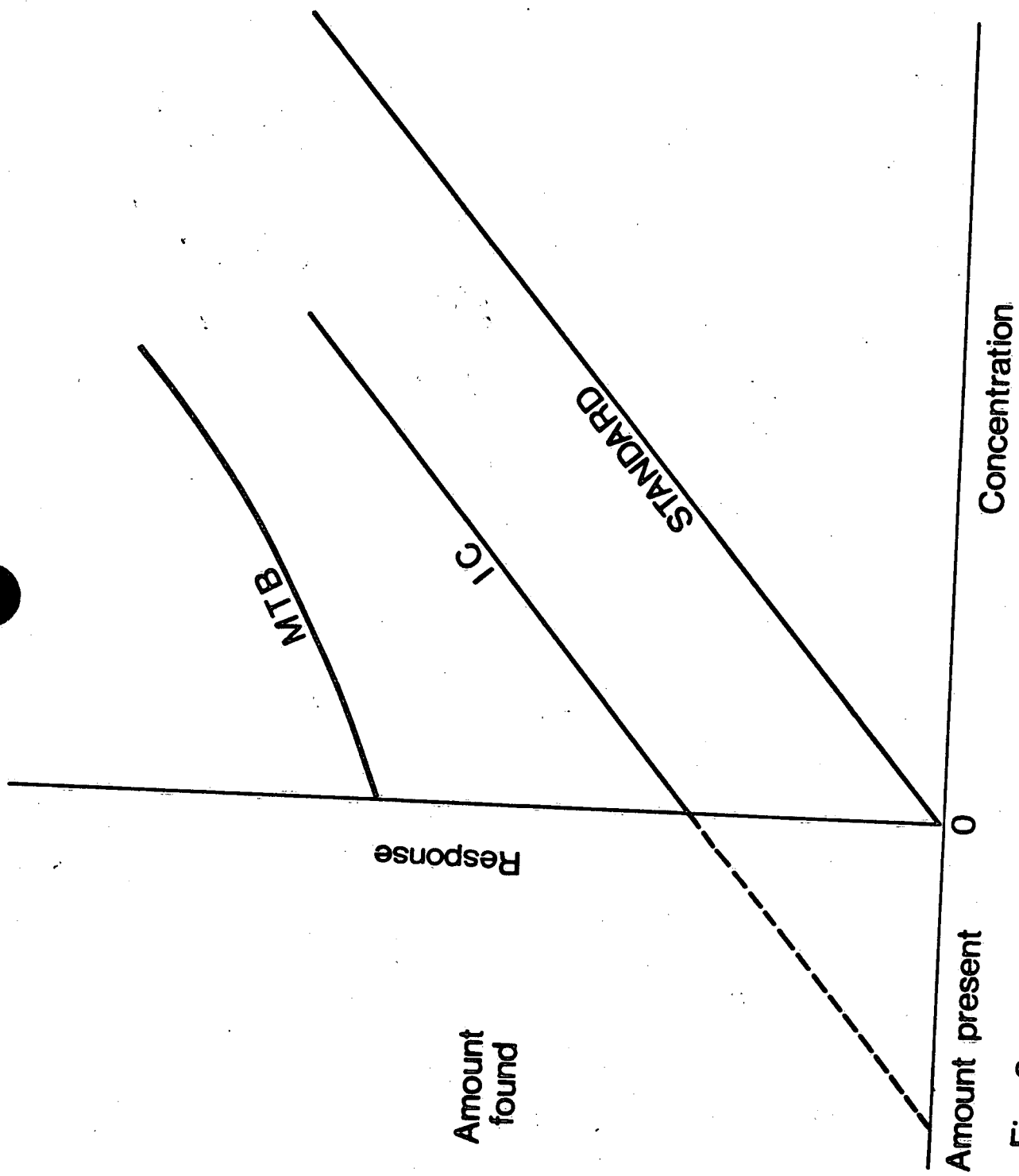


Fig. 2 THE GENERAL BEHAVIOR OF MSA APPLICATION TO THE MTB AND IC METHODS.

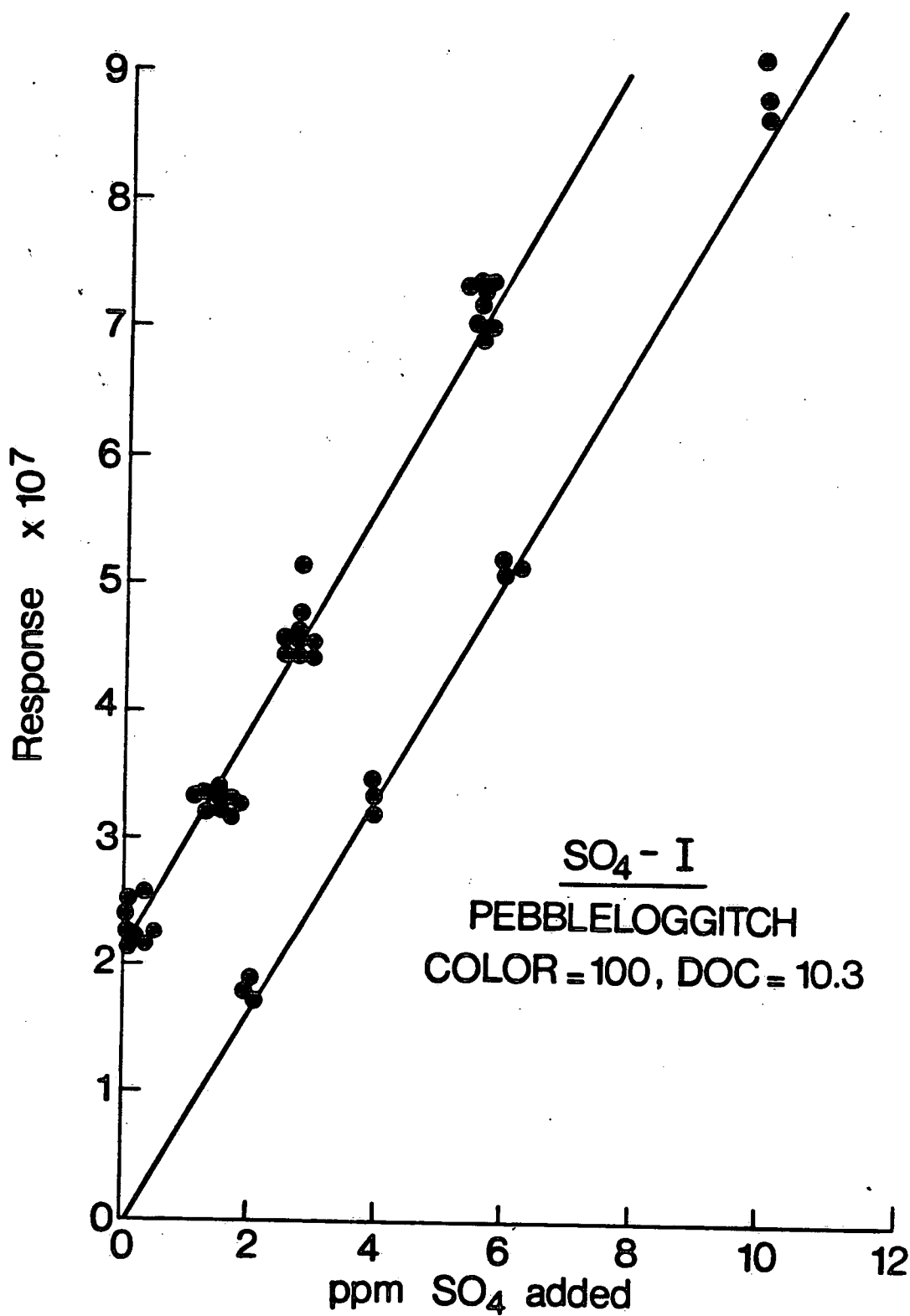


Fig. 3 IC STANDARD ADDITION CURVE FOR SO_4 -I

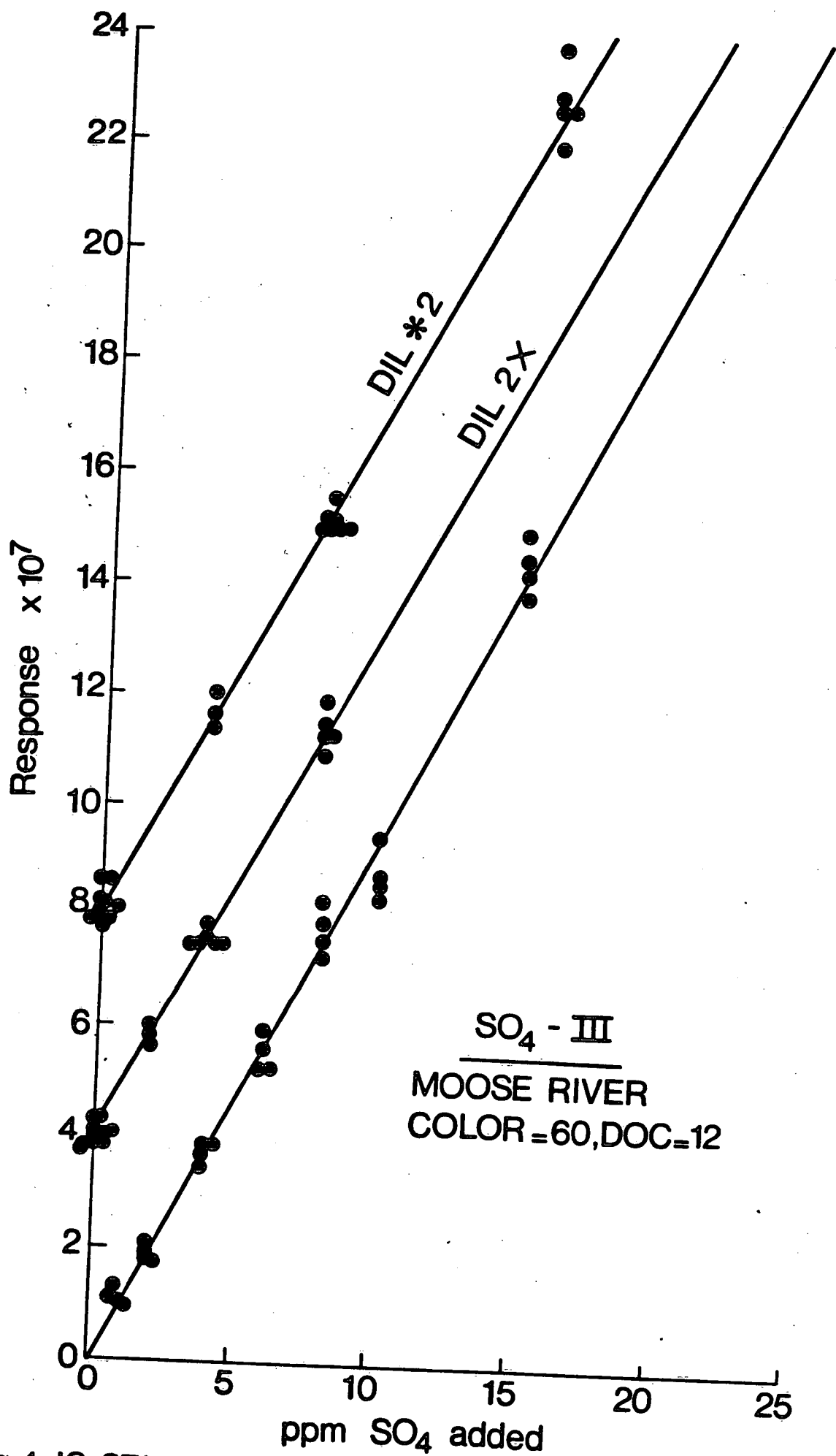


Fig.4 IC STANDARD ADDITION CURVE FOR SO₄-III

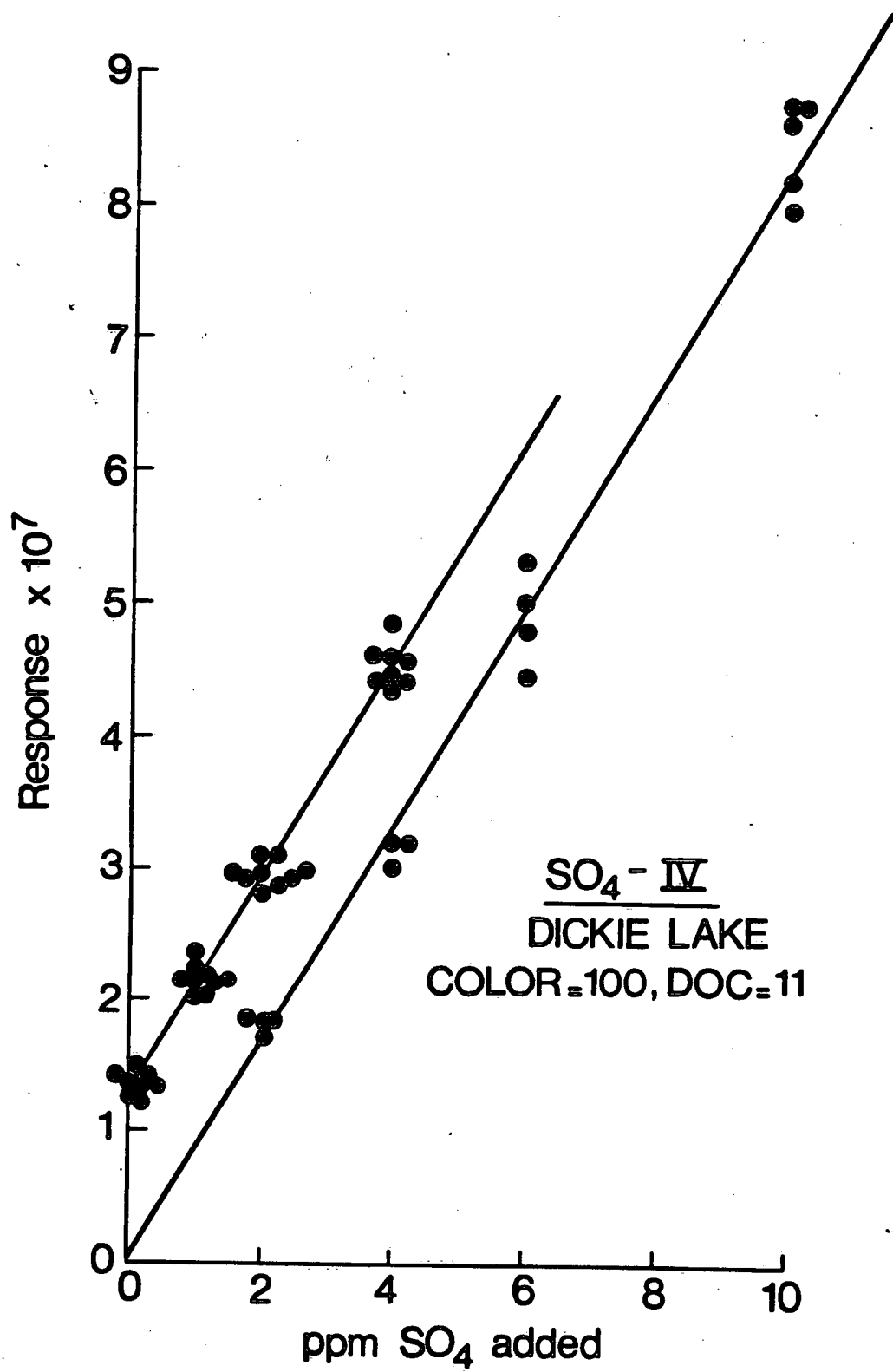


Fig. 5 IC STANDARD ADDITION CURVE FOR $\text{SO}_4 - \text{IV}$

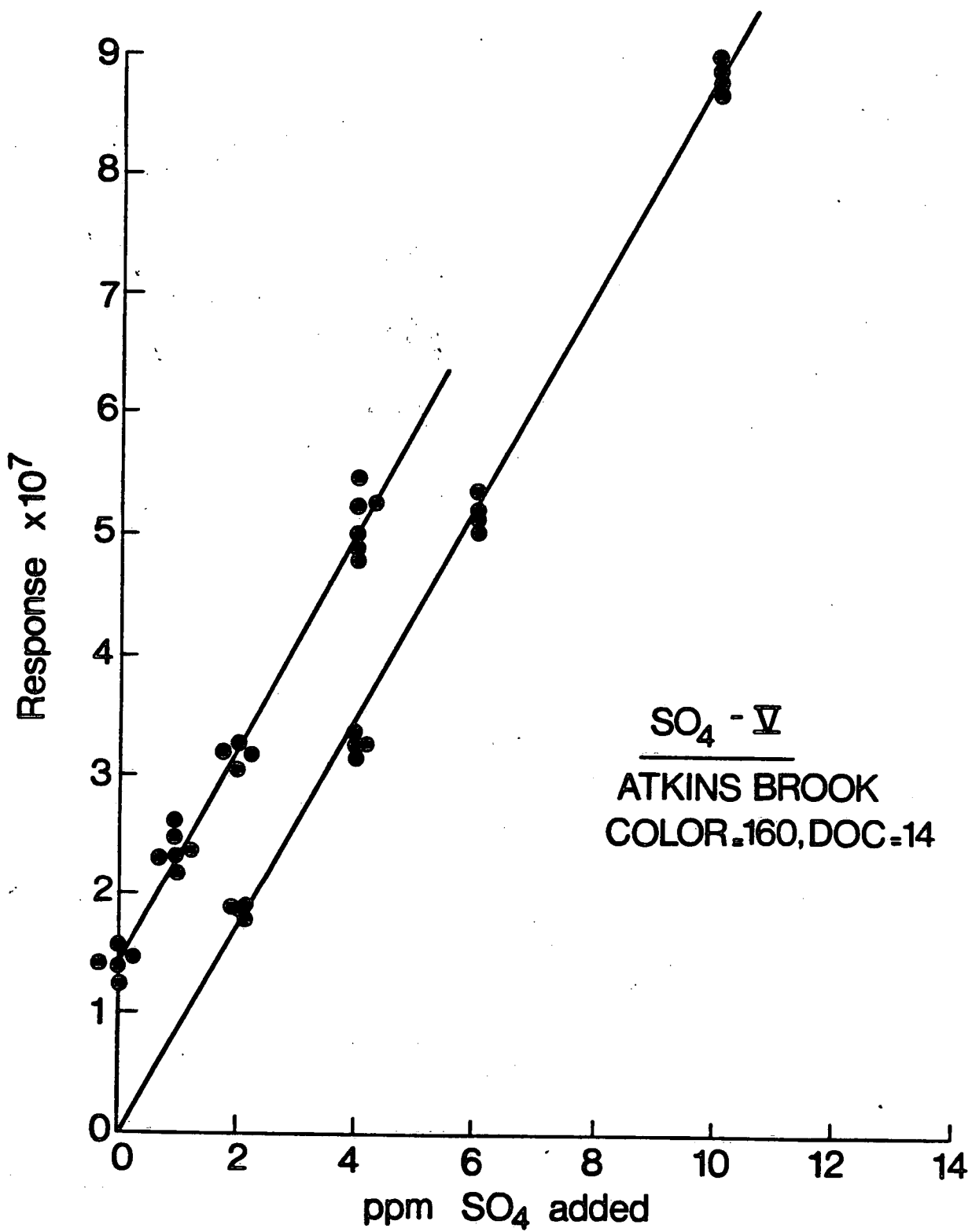


Fig.6 IC STANDARD ADDITION CURVE FOR $\text{SO}_4 - \text{V}$

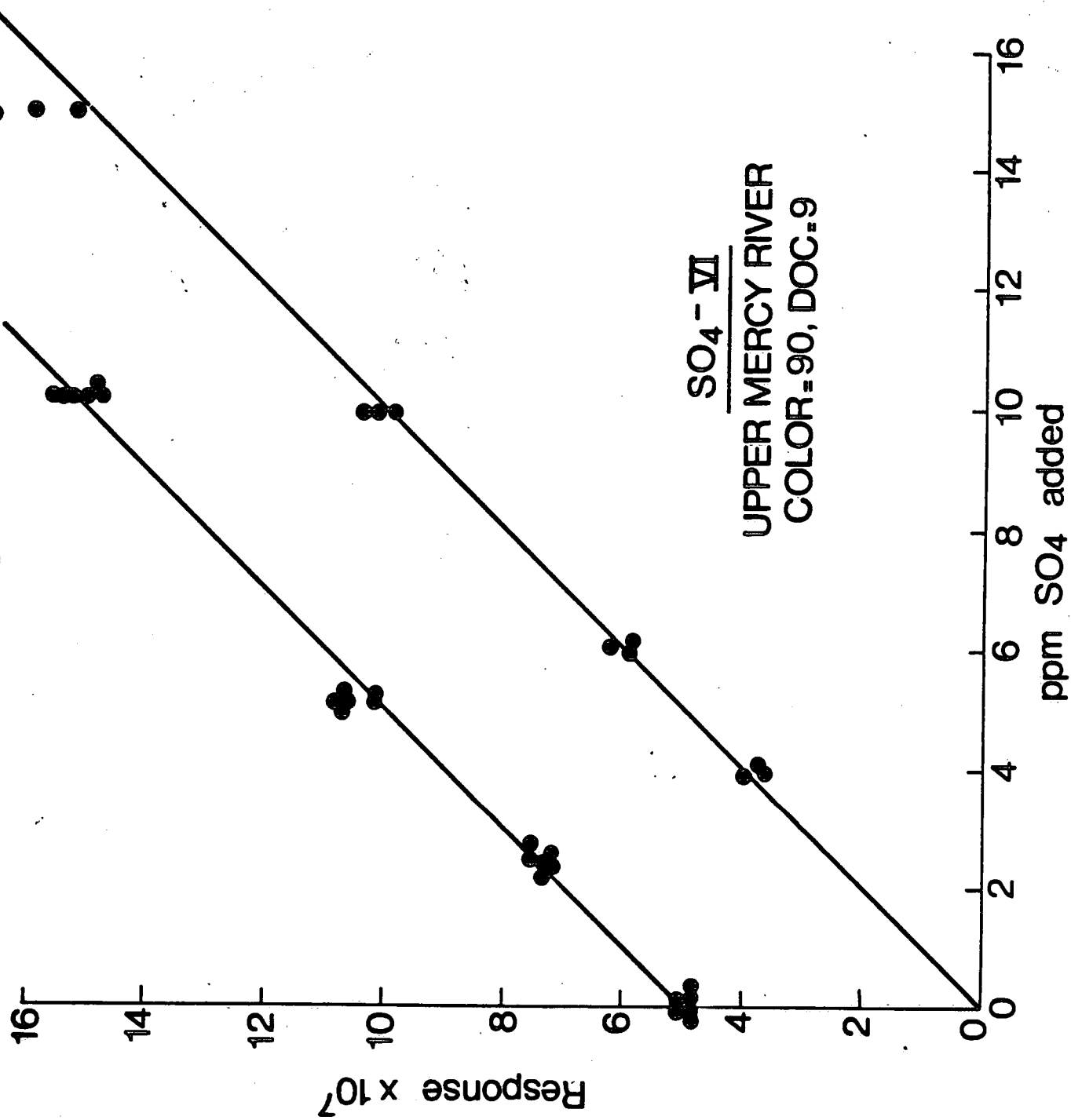


Fig. 7 IC STANDARD ADDITION CURVE FOR SO₄-VI

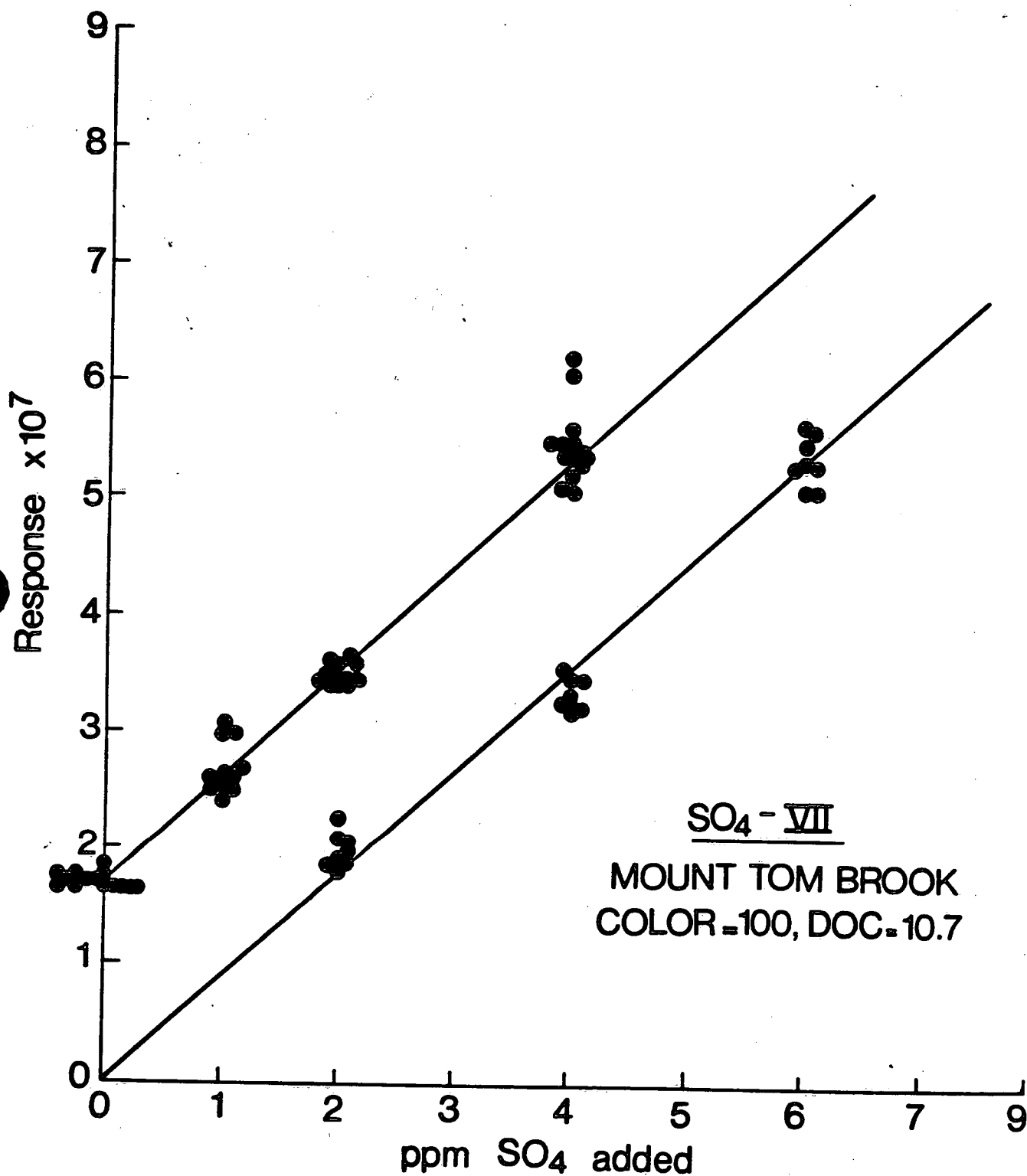


Fig. 8 IC STANDARD ADDITION CURVE FOR $\text{SO}_4 - \text{VII}$

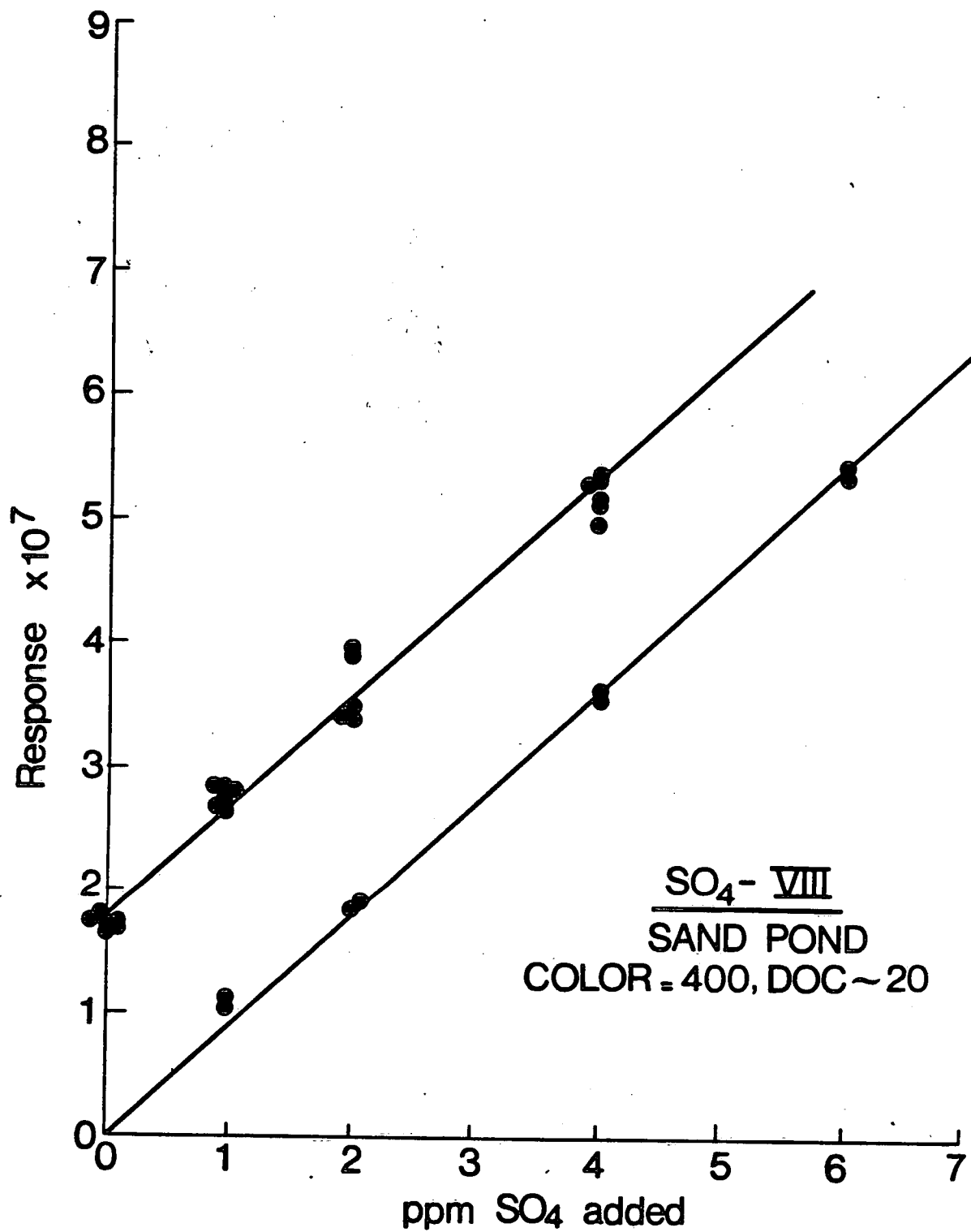


Fig. 9 IC STANDARD ADDITION CURVE FOR SO_4 -VIII

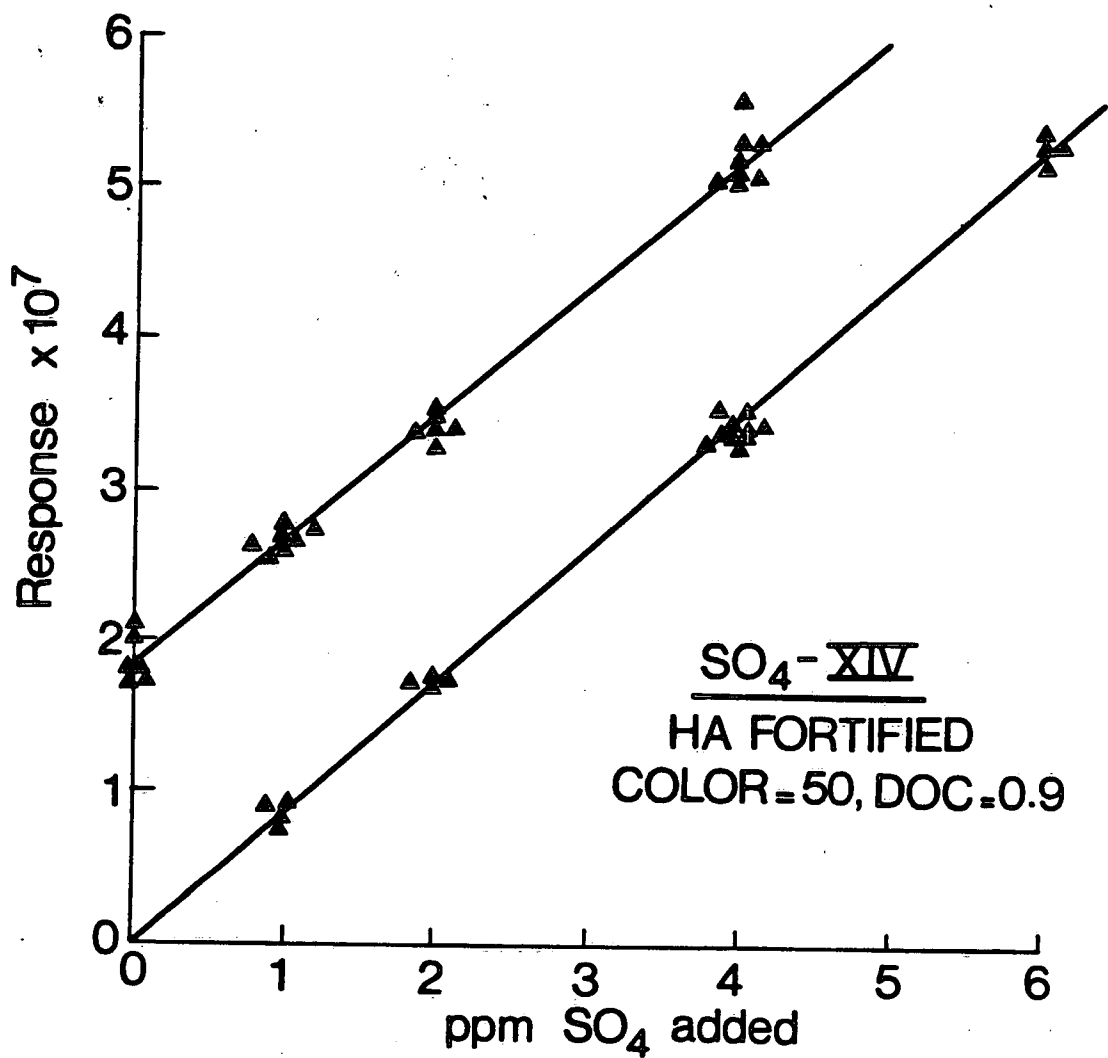


Fig. 10 IC STANDARD ADDITION CURVE FOR $\text{SO}_4\text{-XIV}$

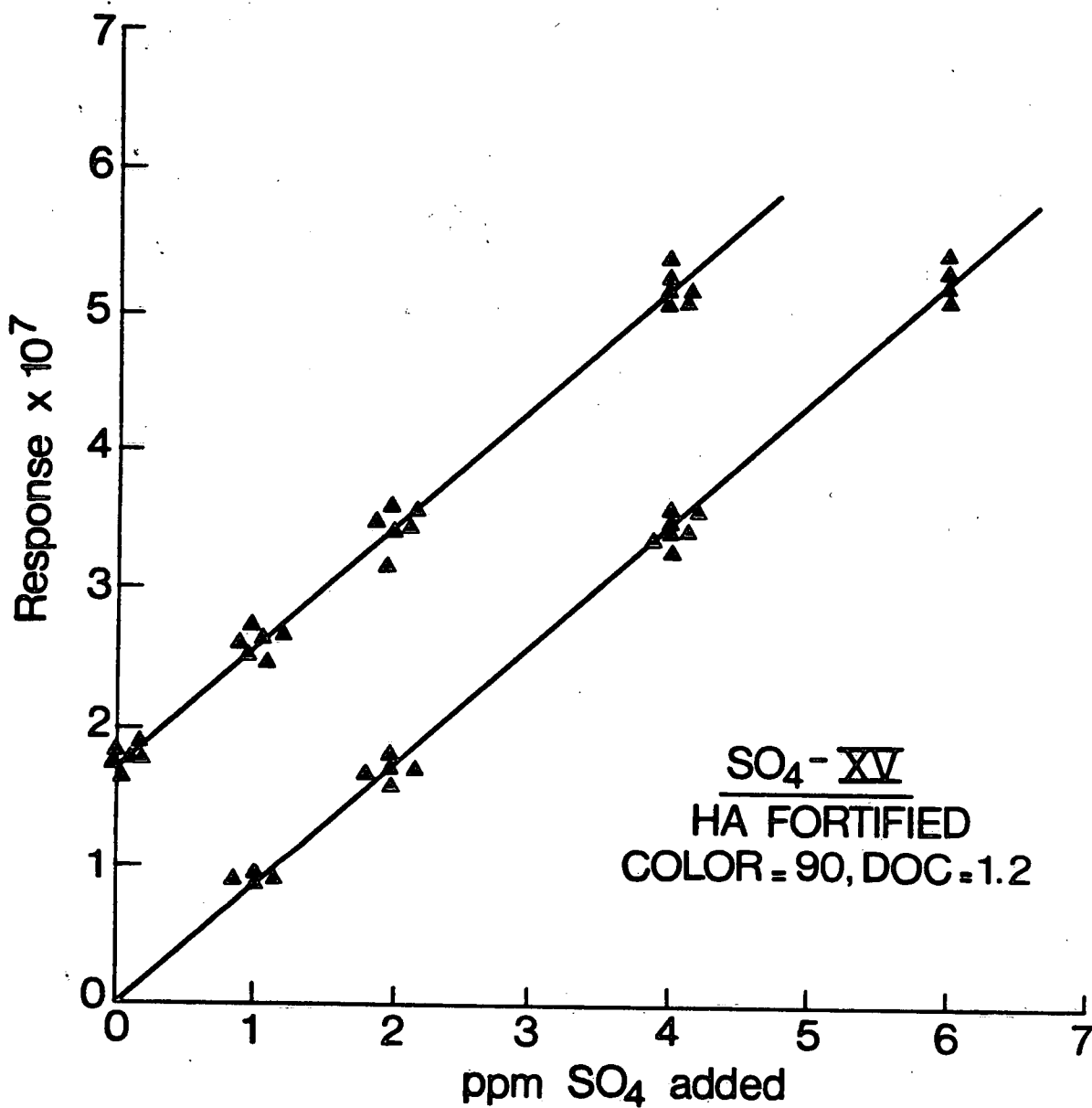


Fig. 11 IC STANDARD ADDITION CURVE FOR SO₄-XV

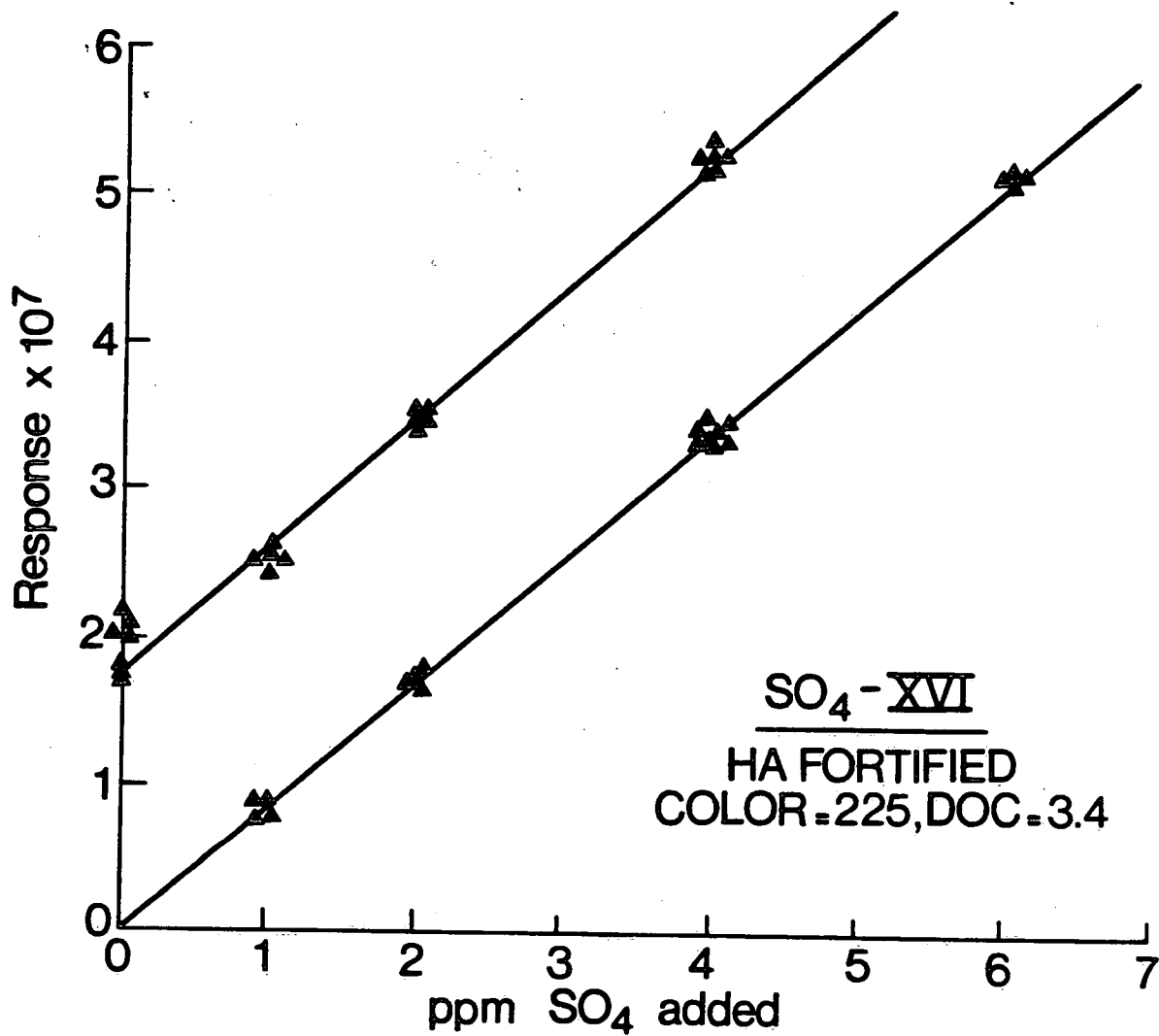


Fig. 12 IC STANDARD ADDITION CURVE FOR $\text{SO}_4\text{-XVI}$

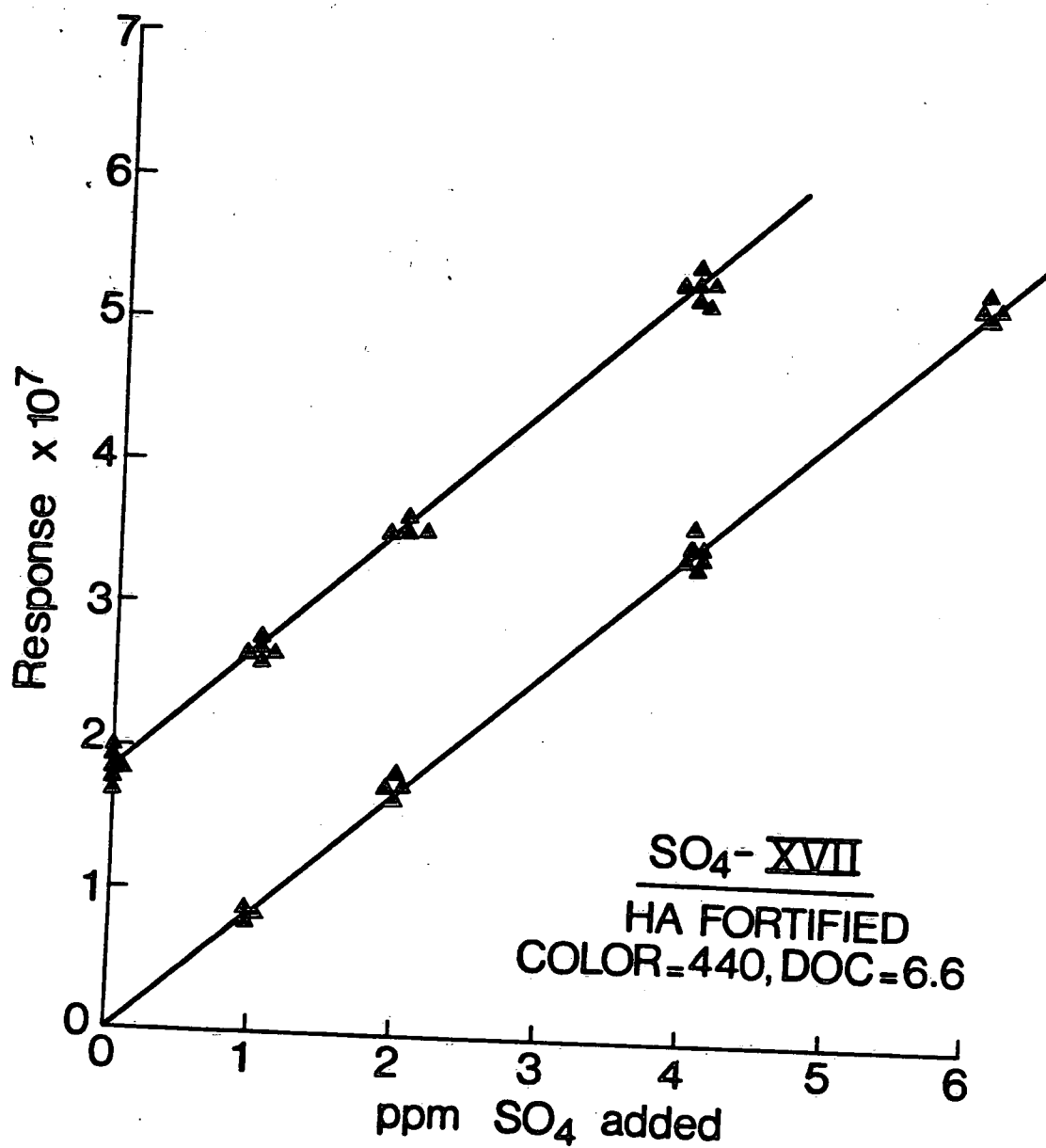


Fig. 13 IC STANDARD ADDITION CURVE FOR SO_4^- XVII

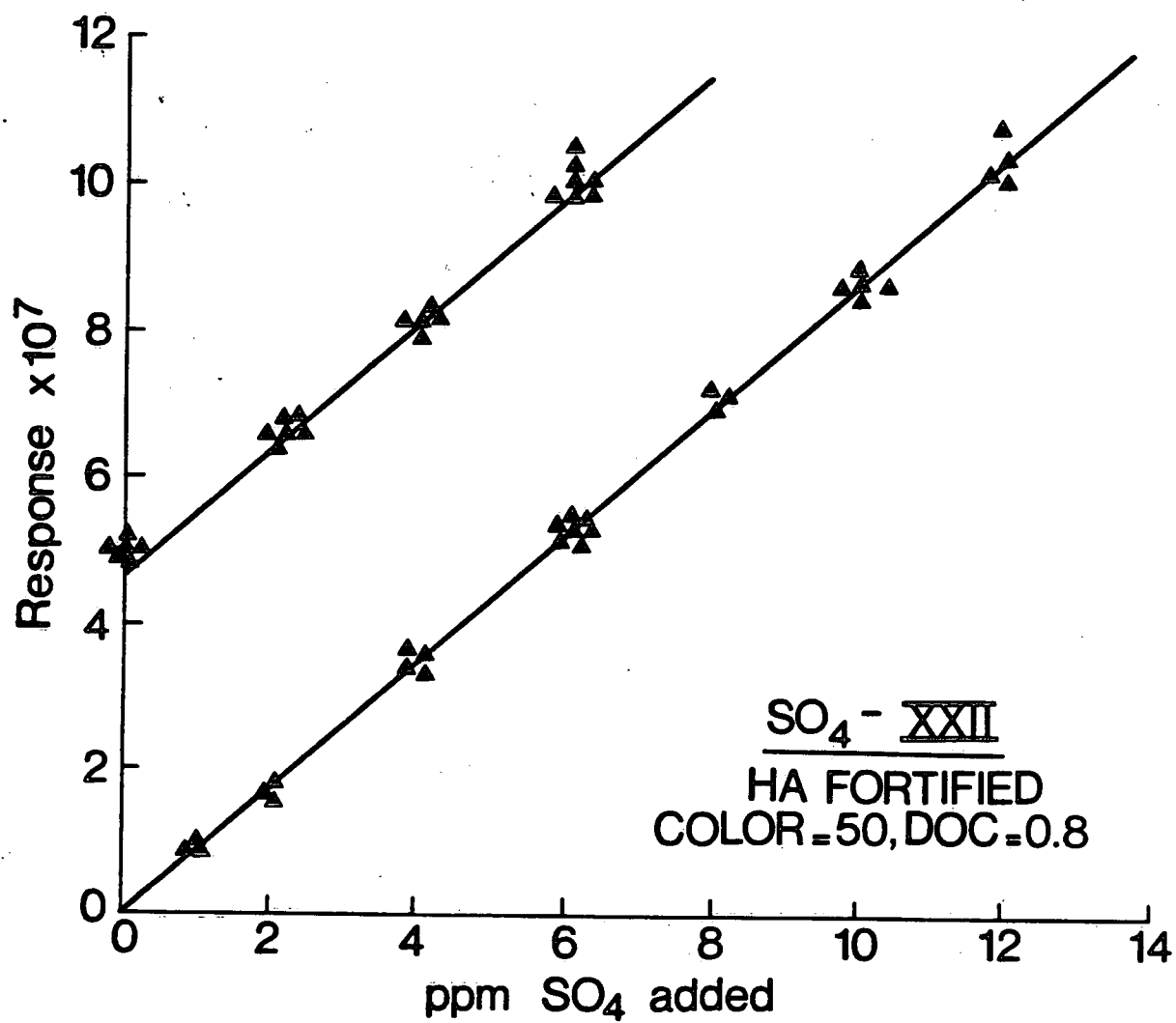


Fig. 14 IC STANDARD ADDITION CURVE FOR $\text{SO}_4 - \text{XXII}$

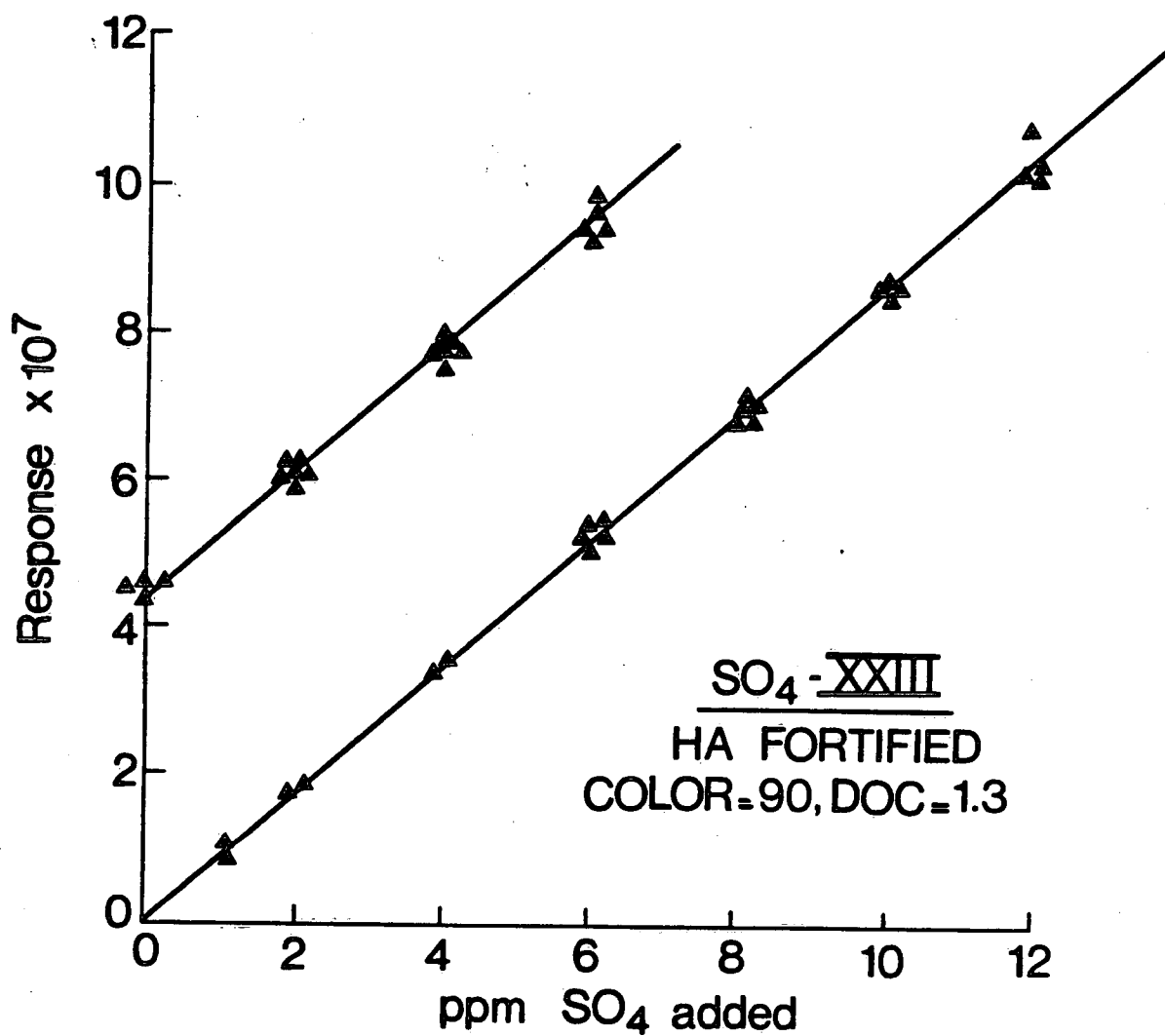


Fig. 15 IC STANDARD ADDITION CURVE FOR SO₄-XXIII

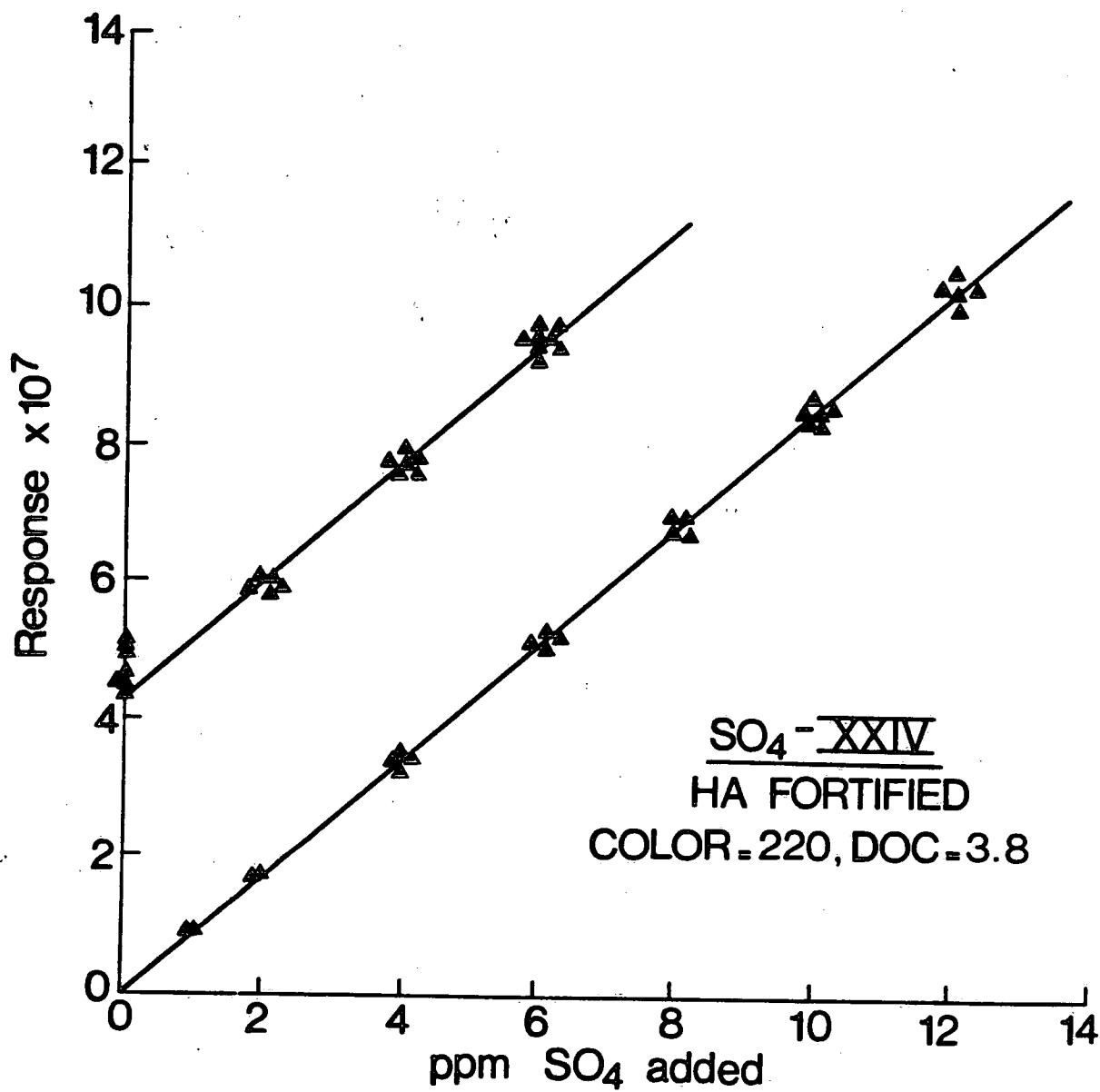


Fig. 16 IC STANDARD ADDITION CURVE FOR SO_4^- XXIV

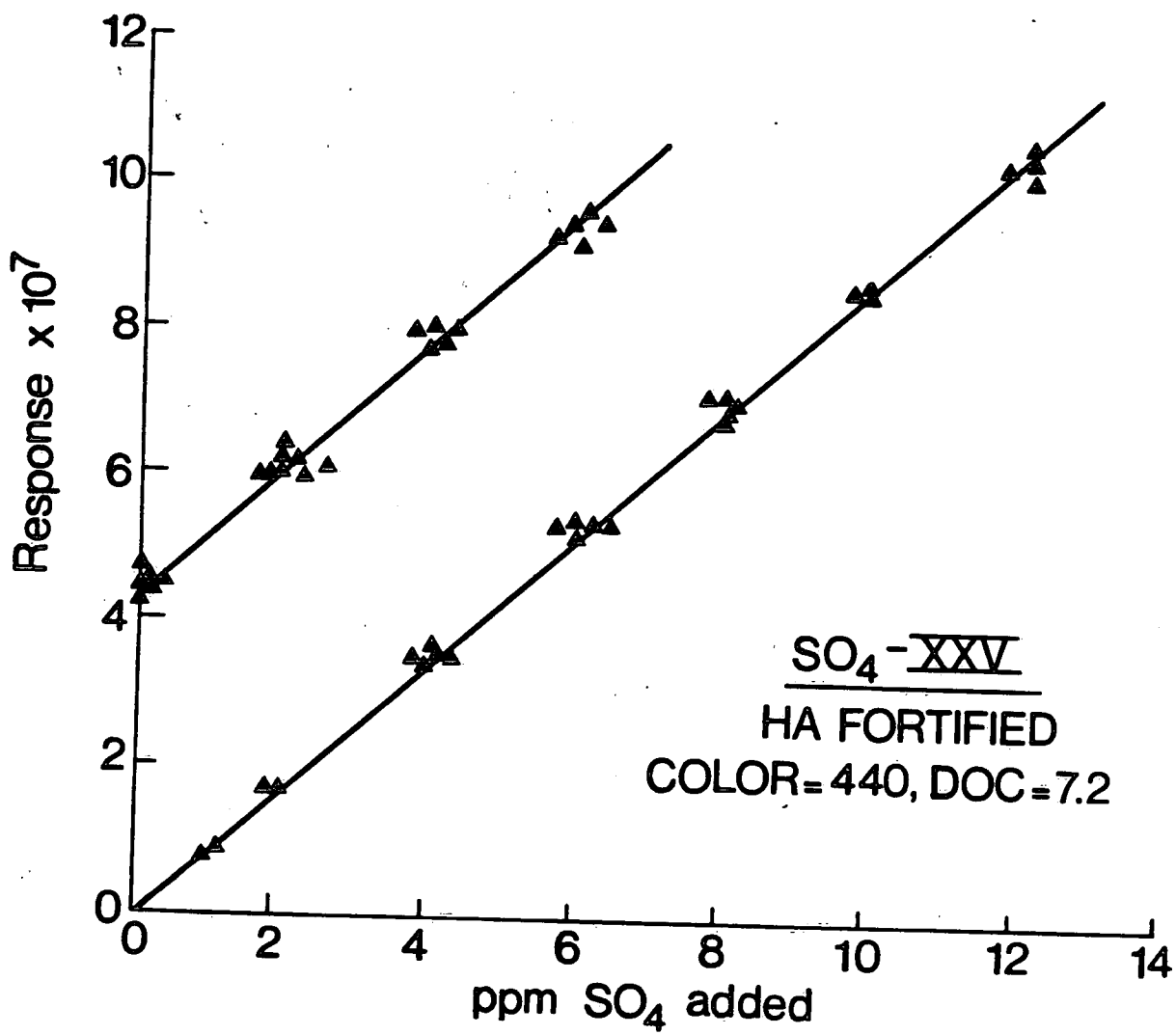


Fig. 17 IC STANDARD ADDITION CURVE FOR SO_4 -XXV