SULFATE IN COLORED WATERS: INVESTIGATION ON
METHODOLOGIES, DATA RELIABILITY, AND
APPROACHES FOR SALVAGING HISTORICAL
COLORIMETRIC DATA

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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 examines in detail several important aspects of the analysis of sulfate in coloured waters. These aspects are analytical methodologies, data reliability, and ways to salvage historical colorimetric data. The data demonstrate that ion chromatography results on organic-contaminated coloured waters are reliable. The study further shows that the colorimetric data are biased high and that it is possible to salvage these types of data through the use of curves having specified amount and nature of organic matter. This approach provides a sure way to correct the historical data and thereby permit data users to interpret the data with confidence.

Dans le domaine de l'étude des pluies acides, l'analyse des sulfates en général, et plus particulièrement dans les eaux colorées, a suscité maintes discussions et préoccupations. La présente étude a été menée à la demande de la Direction générale de la qualité des eaux, Administration centrale, dans le but d'évaluer la méthode colorimétrique et la chromatographie ionique comme moyens de déterminer la concentration de SO_4 dans l'eau colorée.

On se penche sur plusieurs aspects importants de l'analyse des sulfates dans les eaux colorées, soit les méthodes analytiques, la fiabilité des données et les moyens dont on dispose pour récupérer les données colorimétriques historiques. Les résultats prouvent que la chromatographie ionique produit des résultats valables pour l'analyse des eaux colorées contaminées par des substances organiques. L'étude met en évidence un biais positif des données colorimétriques. Ce type d'écart peut être redressé au moyen de courbes établies pour des quantités spécifiques de substances organiques de composition connue. Cette approche est une méthode sûre pour corriger les données historiques; elle permet ainsi aux utilisateurs de ces données de les interpréter en toute confiance.

ABSTRACT

Several important aspects of analysis of sulfate in coloured waters were investigated, namely, methodologies, data reliability and ways to salvage historical data. The multiple standard addition technique was applied to seven natural waters and eight humic acid fortified waters. The colour ranged from 50 to 440 H.U. It was confirmed that the Methyl Thymol Blue (MTB) colorimetric data were biased high. For the first time, it was demonstrated that Ion Chromatography (IC) data on organic-contaminated coloured waters are reliable.

In order to find a way to salvage historical colorimetric data, several approaches were attempted, which related SO_4 data from MTB and IC methods along with colour and organic carbon data. The approaches relating the difference between SO_4 results by MTB and those by IC versus colour, or versus organic carbon, were not completely effective as the magnitude of the true SO_4 content, shown to have a significant role in data interpretation, was not taken into consideration. We have shown that it may be possible to salvage historical colorimetric data through the use of curves, termed "isocarbons", which directly related the magnitude of the true SO_4 value (determined by IC) to that of SO_4 value determined by MTB on waters with specified amount and nature of organic matter.

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INTRODUCTION

There has been a great deal of dicussion and concern over the analysis of sulfate in coloured waters. This is partly due to its importance in the study of acid rain, and partly 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 reported serious incompatibility 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 (T. Pollock, 1981, 1982 and 1983, personal communications; J. Crowther, January 1983, personal communication; Workshop on chemistry of coloured waters (11)). Thus in this study, we wish first to establish the reliability (or non-reliability) of IC data, as well as MTB data. Then we examine the different approaches for salvaging historical colorimetric data.

STUDY DESIGN

Establishing data reliability or validating methodologies 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 first utilizes the principle of multiple standard additions (12-16) to establish whether or not the IC and MTB data are reliable. Then it evaluates the various data handling approaches to best manage historical colorimetric data. For this, we used many different types of organic-contaminated coloured waters and carried out the study in several phases.

Phase I dealt with seven different natural coloured waters from the Atlantic and Ontario regions (Table 1). Phase II dealt with humic acid and fortified coloured waters. In total, there were 14

different fortified samples prepared, each having its own set of variables (Table 2).

By studying the commercial humic acid (Phase II) along with natural organic matter in coloured waters (Phase I), we diversified the types of organic matter studied, and at the same time were able to complement Phase I with test waters having a more even spread of colours (Tables 1 and 2). In the two phases, all samples were analysed by MTB and IC methods.

The third phase dealt with the manual titration using Thorin as indicator of colour change. Some natural samples were utilized to check the performance and usefulness of this method; it was not intended to be an exhaustive examination of the method, but rather to look at its potential as a reliable method. Also, as part of the study design, we included four natural coloured samples in a Long Range Transport of Atmospheric Pollutants (LRTAP) intercomparison study, No. L4 (22).

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 for Phases I and II is schematically presented in Figure 1 where sample SO_4-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 fortified samples SO_4-X to SO_4-XIV (Table 2), the original SO_4 concentrations were found to be very small; subsequently, each was fortified with 2 ppm SO_4 to produce samples SO_4-XIV to XO_4-XVII, and with 5 ppm SO_4 to produce samples SO_4-XXII to SO_4-XXV (Table 2). These fortified values were taken as original approximate concentrations, x_0, of the fortified waters.

Each of the samples was then subsampled according to the scheme in Fig. 1, and each subsample was spiked with SO_4 stock solution to yield a final added concentration equal to 0.5 x_0, 1

x_o and 2 x_o. (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 on SO_4, colour and DOC). Each of these subsamples was further subdivided into smaller subsamples for various analysis.

The original fortifications of 2 and 5 ppm SO_4 (Table 2) were chosen because six out of seven natural samples used in Phase I (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 (Table 1). Also the pH was adjusted to approximately 4.3 so that it is within the usual acid rain pH of 4-5. The Ba spike of ~1 ppm was added to only two samples, SO_4-XXX and SO_4-XXXI (Table 2), to see whether there is any Ba interference or problem associated with its presence. Barium of about 1 ppm was used because a calculation based on solubility products (17) indicates no precipitation of $BaSO_4$ at 2 ppm SO_4.

Analytical Methods

The ion chromatography (IC) analyses of SO_4 were carried out using an automated Dionex 2100 system. All samples were filtered, as in all other analyses, 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, 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 by the Water Quality National Laboratory (IWD) using the automated methyl-thymol 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 (if no interferent exists).

The manual titrimetric method, Naquadat code 16303, used Thorin for the detection of end point (change in colour from yellow to pink) during the titration with $BaCl_2$ solution (18).

Dissolved organic carbon 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.

Definition of Terms

To avoid confusion in subsequent discussions, the key terms are defined as follows:

C = concentration of SO_4

C_{MTB} = concentration of SO_4 determined by colorimetric method using Methyl Thymol Blue as colouring reagent

C_{IC} = concentration of SO_4 determined by Ion Chromatography

ΔC = $C_{MTB} - C_{IC}$

DOC = Dissolved Organic Carbon

HA = Humic Acid

MSA = Multiple Standard Addition.

RESULTS AND DISCUSSION

Validity 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 curve, 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 and the amount found, whereas the abcissa represents the concentration added and the amount "present". The latter is defined as the absolute abcissa value at the intersection of the abcissa line and the extrapolated addition line.

The MTB line (Figure 2) is curved, which indicates, as expected, existence of interference. 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 data for MTB analysis (by direct analysis and MSA). Furthermore, the MTB results are, as expected, higher than 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_o), 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 C_{IC} 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 curves 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 -XIII). This table further shows the agreement between SO_4 amounts determined by direct analysis and by MSA. These amounts represent for all practical purposes 100% of the true value, indicating once again IC reliability.

To find out if the method of standard additions works at higher SO_4 levels and to get more data at these levels, we spiked 5 ppm to each of four HA fortified waters at colour 50, 90, 225 and 440 H.U., and applied the MSA. Figures 14-17 and Table 6 clearly indicate excellent agreement between the three amounts, true-found-present, 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.

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). These results indicate that Ba causes no interference at this level.

ΔC and Colour Relationship

ΔC is defined as the difference between the concentration of SO_4 obtained by the MTB method and the IC method. Figure 18 shows the relationship between ΔC and colour for the data from HA fortified coloured waters (solid squares) and natural coloured waters (solid circles). Each water is represented by two points connected by a vertical line. Each of the points represents the ΔC average of about 6 or more replicate analyses, and is tagged by the corresponding rounded C_{IC} value. As an example, for the water with 160 H.U., the vertical line connects the two points tagged with "2" and "6". The "2" (the lower number) means 2 ppm, the rounded C_{IC} value of the unspiked water, whereas the "6" (the higher number) means 6 ppm, the rounded C_{IC} value of the spiked water.

All the waters, except two -- of colour 90 and 400 H.U., have their points with low C_{IC} values above those with high C_{IC} values. To better see this general behaviour, a line is drawn to represent approximately the low IC values, and another line to represent the high ones (Figure 18). One sees that the low C_{IC} line is distinctly higher than the high C_{IC} line. This observation indicates the following:

1)   The higher the colour, the higher the ΔC, and

2)   The higher the IC values for a given colour, the lower the ΔC.

It seems, therefore, that if one attempts to derive a linear correlation between ΔC and colour, one will mask the effect of C_{IC} magnitude, since at a specified colour, there can be a whole spectrum of ΔC values (Figure 18). This masking effect may explain the difficulty encountered by Kerekes et al. (1), who stated: "..., a general correction procedure based on colour for the historical MTB SO_4 data, except for crude estimates, should not be employed."

For comparison, the data from the LRTAP study no. 4 (22) are also plotted in Figure 18 (four solid triangles). As can be seen, these points fit well into the low C_{IC} line of in-house data.

ΔC and DOC Relationship

Figure 19 shows the relationship of ΔC and DOC. Two distinct behaviours were observed: one for natural waters represented by the circles and one for HA fortified waters represented by the squares. In each case, two lines could be drawn, as was done in Figure 18, one for the low C_{IC} values and the other for the high values. The solid circles for high IC values were omitted in order to clearly show the four circles situated near the abcissa line. These circles are SO_4-III coordinates. The C_{IC} values for SO_4-III are high and this seems to minimize ΔC in spite of a fairly high DOC content of 12 ppm; it is possible that both the high C_{IC} and low colour (60 H.U.) combine to minimize ΔC.

The above discussion suggests that ΔC does not proportionally depend on DOC concentration alone. Instead it's a function of three elements: the true SO_4 magnitude, the amount of organic matter (DOC), and the nature of the organic matter. The latter element involves the types of chelating sites or complexing capacity of the organic matter (20, 21), and should determine the extent of chemical reaction competing for Ba against MTB at pH ~13. Figure 19 in this study gives a good illustration of this type of competitive reaction. The figure does imply that HA organic matter is a superior competitor by producing higher ΔC than the organic matter in the natural waters

used. Cheam and Gamble (20) compared some of the common chelating agents, including fulvic acid, and found large differences in strength between them.

In Figure 19, the LRTAP interlaboratory data are shown represented by four triangles. As can be seen, they belong to the low IC line of natural waters, indicating agreement with in-house data.

ΔC (or ratio, C_{MTB}/C_{IC}) and C_{IC} Relationship

We have seen that the magnitude of C_{IC} contributes to the variation of ΔC. To illustrate this point further, we relate ΔC and C_{IC} for natural waters (Figure 20). Three distinct curves may be drawn as shown at three DOC levels -- 20, 14 and 9-11 ppm. For synthetic waters well defined curves show up, each at a specific level of DOC 7.2, 3.9, 1.25 and 0.7 ppm (Figure 21). To render future discussions clearer, we shall refer to these curves having specific amount and nature of dissolved organic carbon as "isocarbons" (like in isotherms and isobars).

Combining the latter two figures into one figure (Figure 22), one further appreciates the different curvatures of isocarbons. But the common general behaviour of isocarbons indicates a decrease

as C_{IC} increases, that is C_{MTB} approaches C_{IC} as the latter increases. Figure 22, besides showing that ΔC depends on both C_{IC} and colour (or DOC), further indicates that one can't really generalize about ΔC approaching zero below a certain colour value without also considering C_{IC} magnitude.

To better appreciate this C_{IC} dependence, we plotted the ratio, R ($\equiv C_{MTB}/C_{IC}$) against C_{IC} (Figures 23 and 24). The plots readily reveal R approaching "1" (that is C_{MTB} = C_{IC}) as C_{IC} increases.

In Figures 20 and 23 are also plotted the LRTAP inter-laboratory data on four coloured waters. The water with colour 155 H.U. is represented by the solid squares, whereas the three other waters with a colour range 79-100 H.U. by the solid triangle. Overall, these points are well within the spread of in-house data.

C_{MTB} and C_{IC} Relationship

Figures 25 and 26 illustrate the relationship between C_{MTB} and C_{IC} data. In these figures, we again represent the points having similar amount and nature of DOC by isocarbons. As can be seen, some isocarbons are well defined, but others are not. This is probably due to the ever present errors in any analytical data. In

this case, the errors are from C_{MTB}, C_{IC} and DOC analyses by different labs and different operators. The net effect of combined errors would make it impossible to distinguish the results which are within 10-20%. For example in Figure 26, it would be impossible to differentiate the curve representing the x's from those representing the o's, Δ's and 's; one has to treat them as belonging to the same isocarbon, which we will do below.

In Figure 25, the points appear to be better separated than those of Figure 26. This is due, by design, to the more evenly spread DOC values and the identical nature of organic matter associated with the four isocarbons. Even then, the analytical errors mentioned above make the spread of points for each isocarbon fairly large and the two lower curves (DOC = 1.25 and 0.7) more difficult to differentiate.

In spite of the analytical errors, Figures 25 and 26 along with 22 do show definite existence of many different and well defined isocarbons. This suggests that it would be virtually impossible to salvage historical data with a simple correction factor. One would have to group similar waters and treat them separately.

As an example, one set of waters has DOC of 10 1 ppm and colour 80-110 H.U. (Figure 26). We have replotted all the points

associated with these waters with open circles as shown in Figure 27. Also plotted in this figure are the solid circles, which represent the average interlaboratory data on three different natural waters used in a LRTAP quality control study, L_4 (22). The interlaboratory DOC ranged from 8.8 to 11.5 ppm, whereas the colour ranged from 79 to 100 H.U. Considering all the points, a representative isocarbon may be drawn through them and may be described by the following $C_{MTB}-C_{IC}$ relationship.

$$C_{MTB} = 3.05 + 0.66 (C_{IC}) + 0.009 (C_{IC})^2.$$

In Figure 27, the isocarbon with 10 ± 1 ppm DOC reveals several things:

a) the effect of C_{IC} magnitude -- as C_{IC} increases, the isocarbon becomes more and more like the 1-1 line, the uncontaminated water line. To further illustrate the C_{IC} effect, we plotted in solid triangles the data from the natural water having 12 ppm DOC. In spite of this fairly high DOC, the water's high C_{IC} values (> 9 ppm) produced points which basically straddled the 1-1 line, that is C_{MTB} ~ C_{IC}.

b) it may be deduced that the nature of the organic matter for these waters are similar.

c)   it permits direct conversion of colorimetric SO_4 to "true" SO_4 data on waters having similar amount and nature of organic matter.

d)   it may be deduced that other C_{MTB} - C_{IC} isocarbons can be constructed for other types of waters, case by case, and can be used to salvage historical MTB data on those types of waters.

Kerekes (personal communication, 1984) correlated colour and DOC and found the two parameters linearly dependent on each other. If this is the case, at least for the waters from the Atlantic Region, then the isocarbons become identical to curves having specified colours, which may be termed "isochromes". It follows from Kerekes' concept that those MTB historical data with accompanied colour determinations can also be salvaged. However, we note that the present study indicates non-correlation between colour and DOC when dealing with different nature of DOC.

Thorin manual titration

The manual titration method (18), relative to MTB and IC methods, is a more tedious technique to use and its performance is very much influenced by the analyst's subjective judgement. The analyses can be easily biased or imprecise due to the difficult end

point detection and the errors from burrette readings, particularly when analysing low SO_4 levels in coloured waters. Furthermore, the method is time consuming and requires the constant attention of the analyst. Therefore, it's not a preferred technique in a modern analytical service laboratory.

The method, however, performs better than the MTB technique in the analysis of coloured waters. With much care and practice, it is possible to produce titration results close to IC analyses. Table 7 compares the analytical results from both methods using a new batch of coloured water samples.

CONCLUSIONS AND RECOMMENDATIONS

Numerous SO_4 data on coloured and organically contaminated waters were generated by ion chromatography and MTB colorimetry methods, using multiple standard addition technique. The following are the main conclusions:

1) Ion chromatography (IC) data proved to be reliable.

2) There is no simple and universal correction factor which readily converts the historical colorimetric (MTB) data to true SO_4 values.

3) There may be a general way, however, to handle these data. We are suggesting the use of C_{MTB}-C_{IC} isocarbons, case by case, to salvage historical colorimetric data.

4) The Thorin manual titration is less precise and less rugged than IC technique. The titration, though capable of giving more accurate data than the MTB method for organic-contaminated waters, requires constant and meticulous quality control.

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TABLE 1. IDENTIFICATION OF NATURAL SAMPLES

Sample Name	Origin	Colour	Collected Through
SO_4-I	Pebbleloggitch, Atlantic Region	100	T. Pollock & J. Kerekes
SO_4-III	Moose River, Ontario Region	60	R. MacCrae, Surveillance and Monitoring
SO_4-IV	Dickie Lake, Ontario Region (Dorsett area)	100	M.P. Campbell, MOE
SO_4-V	Atkins Brook, Atlantic Region	160	J. Kerekes & T. Pollock
SO_4-VI	Upper Mercy River, Atlantic Region	90	J. Kerekes & T. Pollock
SO_4-VII	Mount Tom Brook, Atlantic Region	100	J. Kerekes & T. Pollock
SO_4-VIII	Sand Pond Atlantic Region	400	J. Kerekes & T. Pollock

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 ± 0.175	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

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

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 (Amount Found)	MSA (Amount Present)
SO_4-X	0.056 ± 0.033	
SO_4-XI	0.06 ± 0.02	
SO_4-XII	0.08 ± 0.02	
SO_4-XIII	0.111 ± 0.02	
SO_4-XIV	2.17 ± 0.15	2.19 ± 0.19
SO_4-XV	2.09 ± 0.075	2.03 ± 0.054
SO_4-XVI	2.20 ± 0.19	2.09 ± 0.18
SO_4-XVII	2.07 ± 0.02	2.05 ± 0.05
SO_4-XXX	2.07 ± 0.026	
SO4-XXXI	2.18 ± 0.031	

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 ± 0.085	5.54 ± 0.15
SO_4-XXIII	5.09 ± 0.07	5.03 ± 0.016
SO_4-XXIV	5.16 ± 0.03	5.05 ± 0.1
SO_4-XXV	5.09 ± 0.06	5.06 ± 0.17

TABLE 7. COMPARISON OF TITRATION AND IC DATA (± STANDARD
         DEVIATION)

Water	Titration	IC
Pebbleloggitch	2.38 ± 0.24	3.05 ± 0.05
Moose River	11.92 ± 0.60	11.34 ± 0.38
Dickie Lake	4.89 ± 0.29	3.78 ± 0.10
Atkins Brook	1.25 ± 0.21	1.94 ± 0.01
Upper Mercy	10.11 ± 0.28	9.46 ± 0.21
Mount Tom Brook	2.44 ± 0.31	2.18 ± 0.07
Sand Pond	1.59 ± 0.22	2.46 ± 0.21
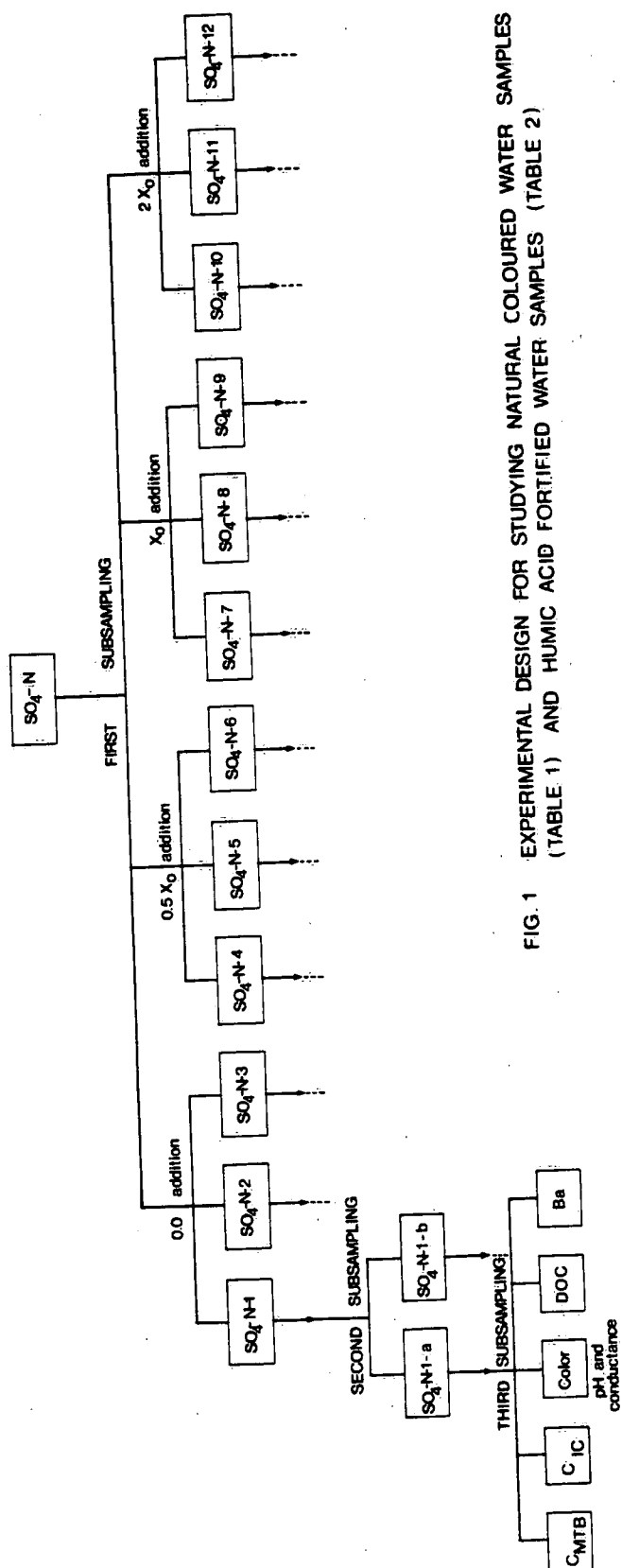
FIG. 1   EXPERIMENTAL DESIGN FOR STUDYING NATURAL COLOURED WATER SAMPLES
(TABLE 1)   AND HUMIC ACID FORTIFIED WATER SAMPLES   (TABLE 2)
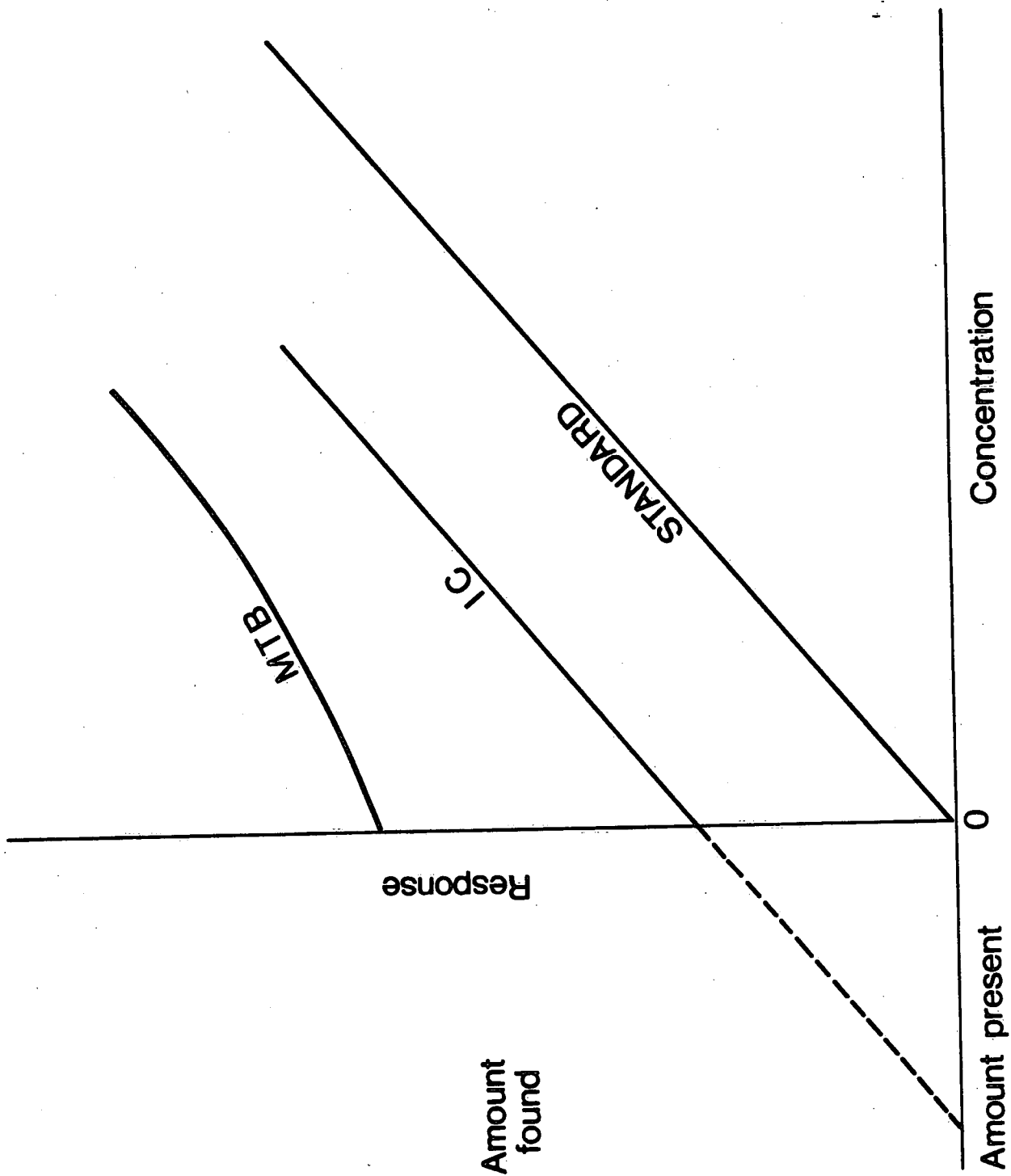
Fig. 2   THE GENERAL BEHAVIOR OF MSA APPLICATION TO THE
         MTB AND IC METHODS.
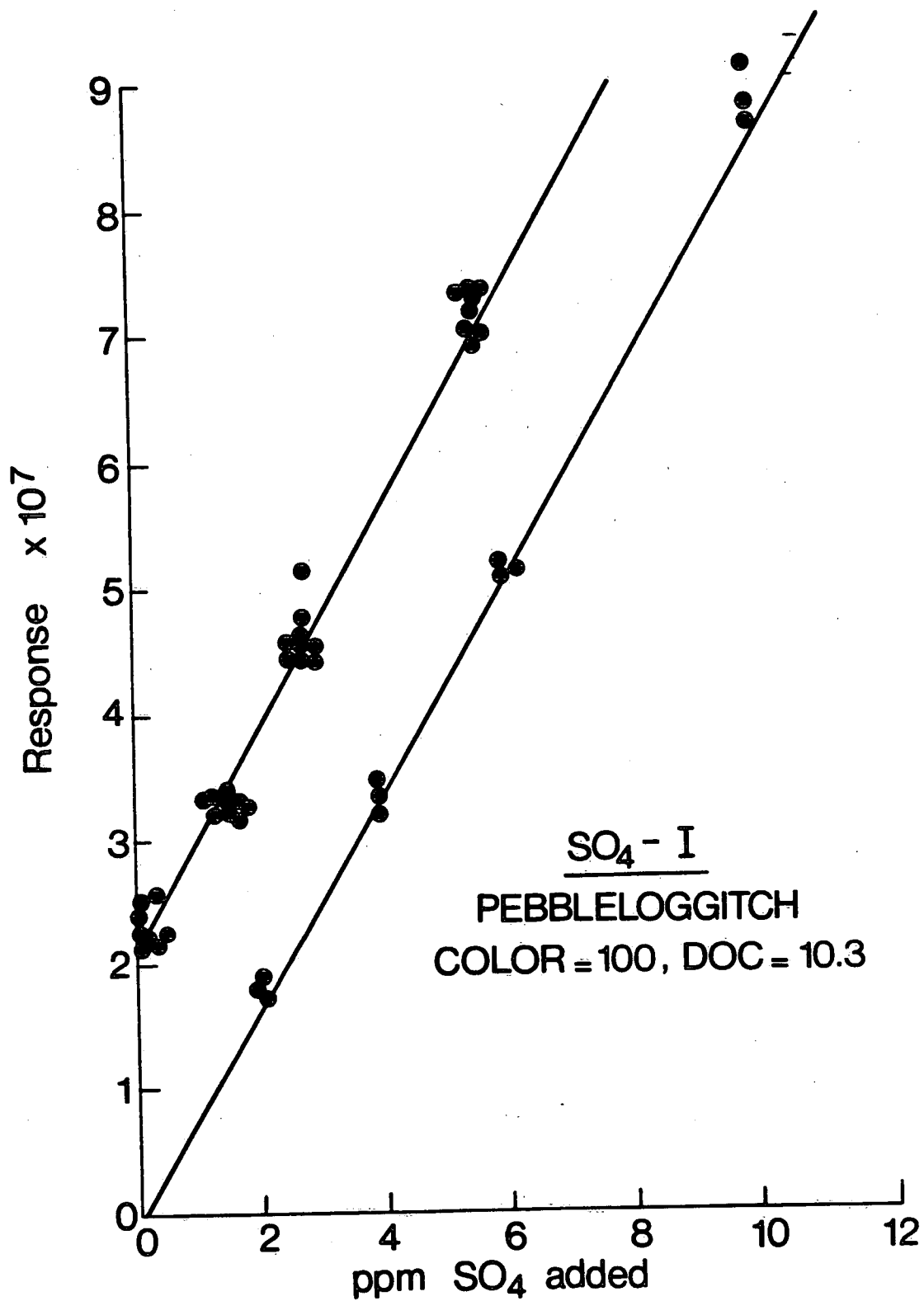
Fig. 3 IC STANDARD ADDITION CURVE FOR SO₄-I
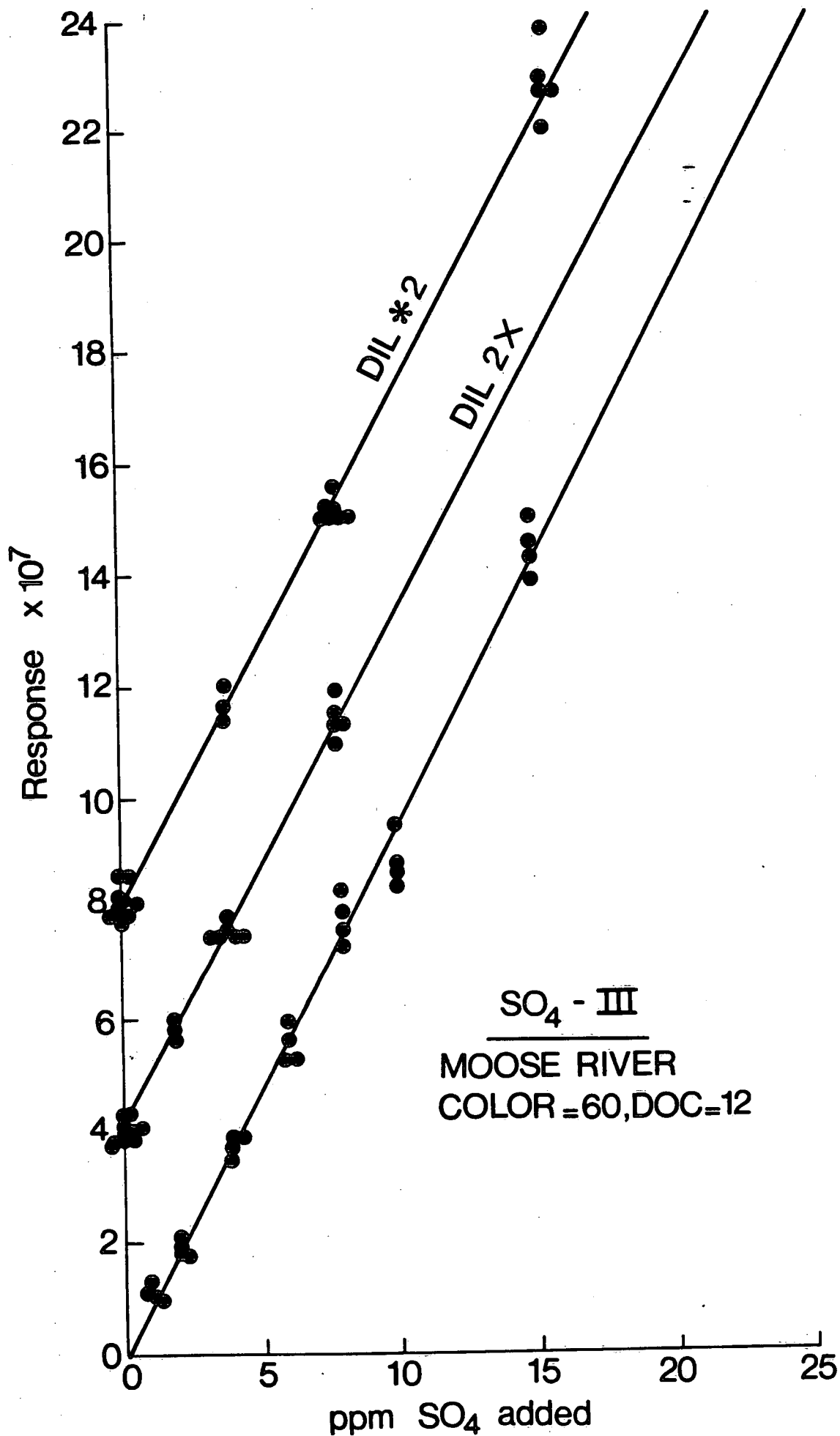
Fig. 4 IC STANDARD ADDITION CURVE FOR SO$_4$-III
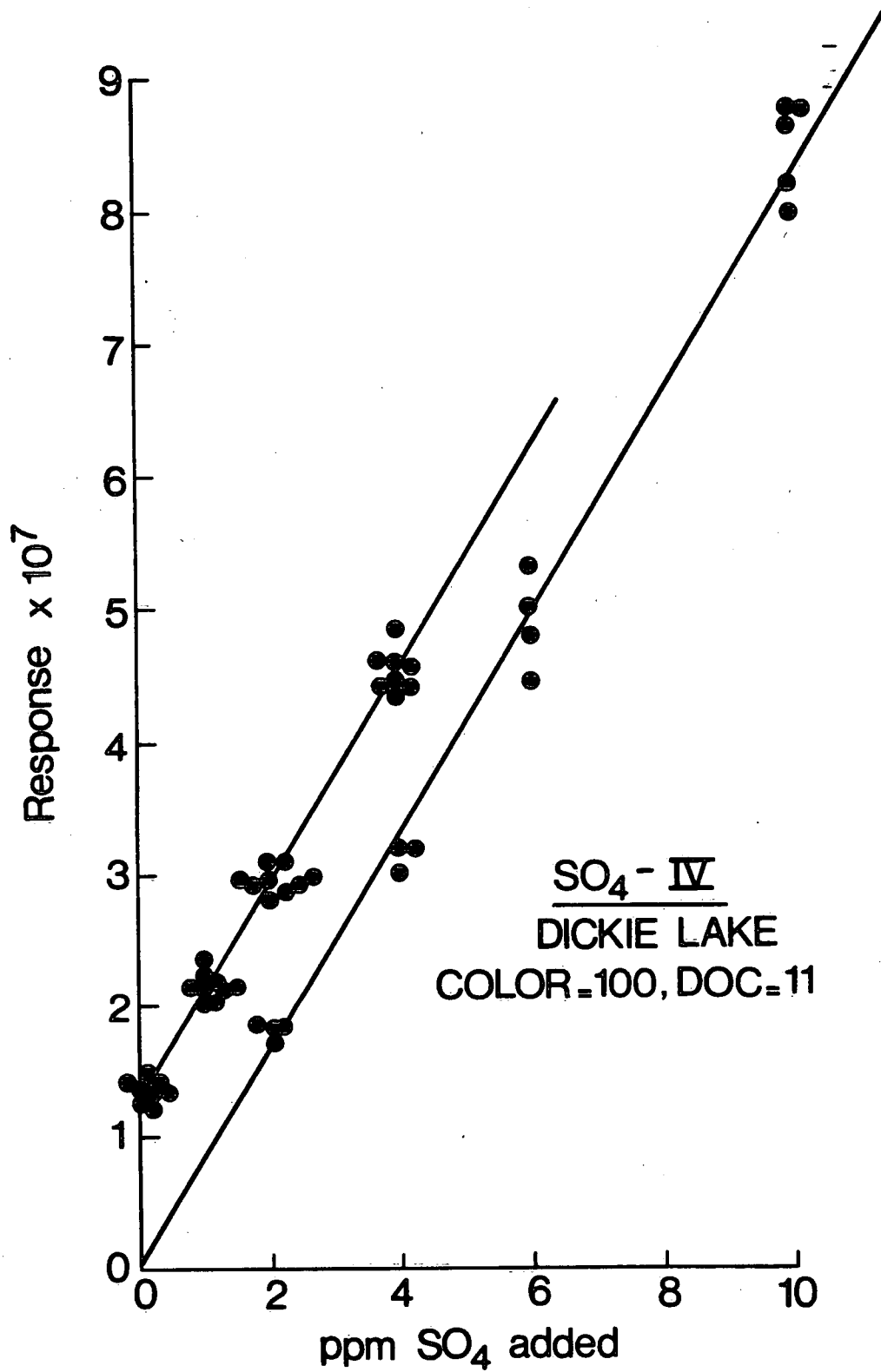
Fig. 5   IC STANDARD ADDITION CURVE FOR SO$_4$-$\overline{\text{IV}}$
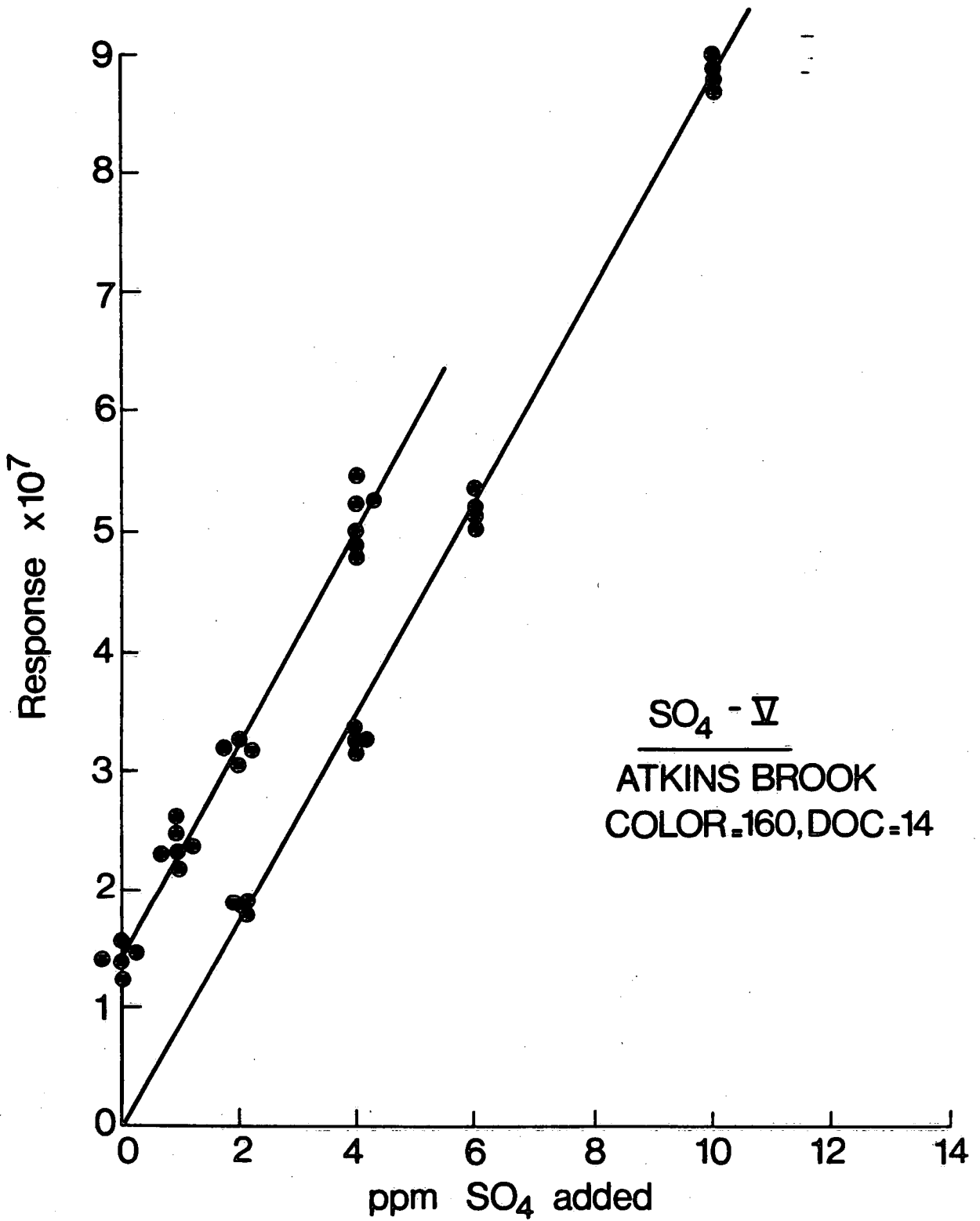
Fig. 6   IC STANDARD ADDITION CURVE FOR SO$_4$- $\underline{V}$
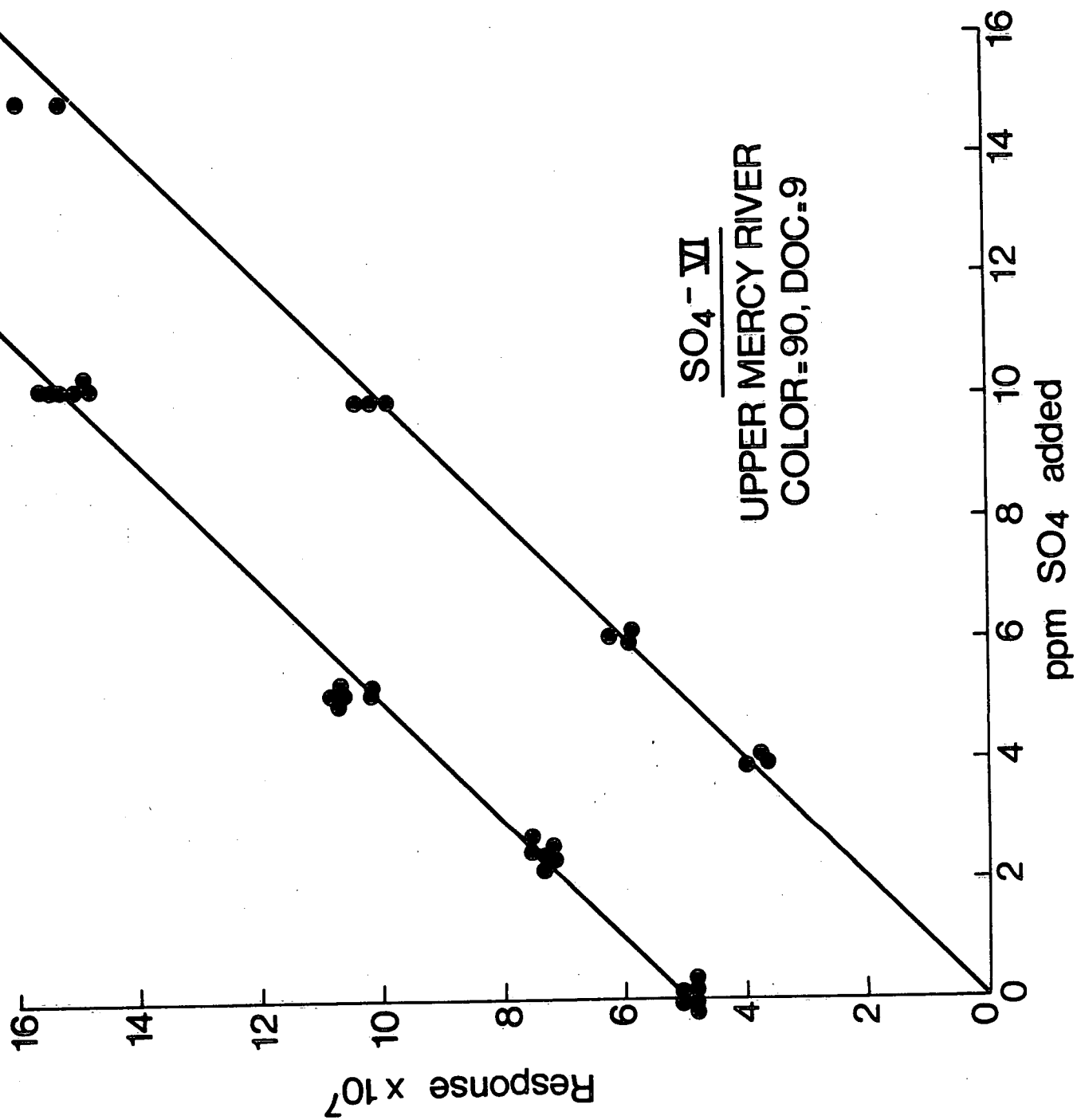
Fig. 7 IC STANDARD ADDITION CURVE FOR SO₄-VI
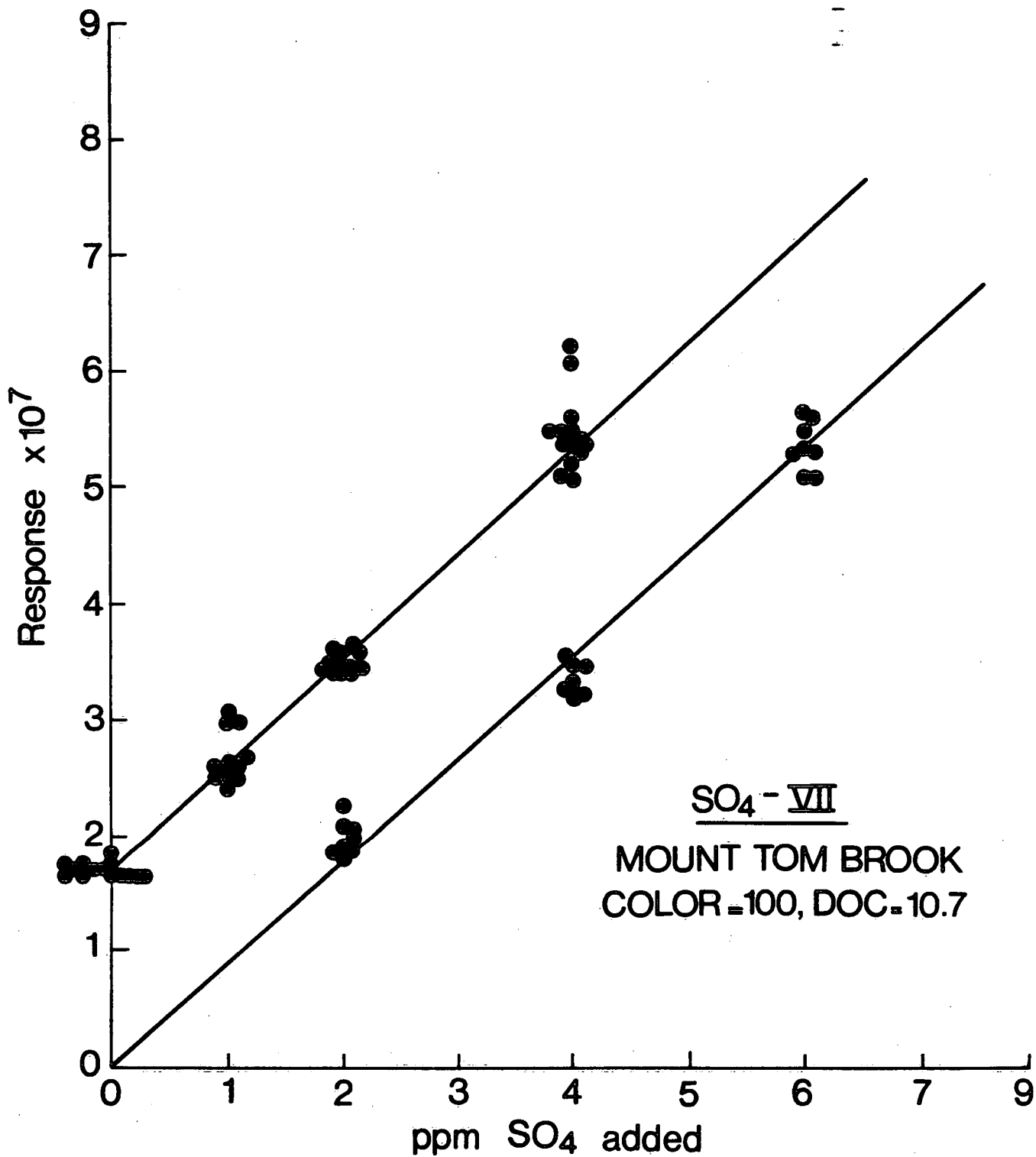
Fig. 8   IC STANDARD ADDITION CURVE FOR SO$_4$-VII
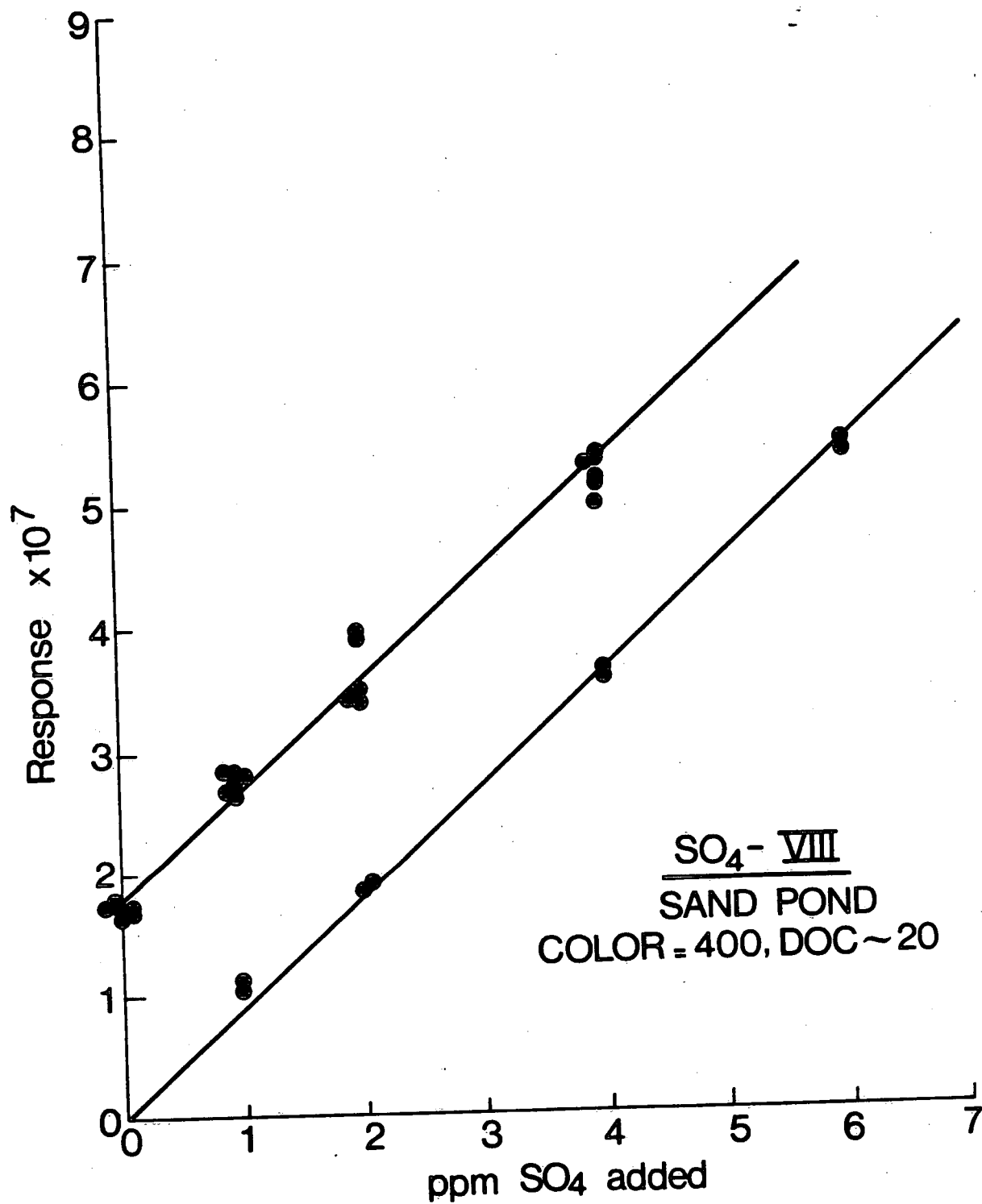
Fig. 9   IC STANDARD ADDITION CURVE FOR SO_4-VIII
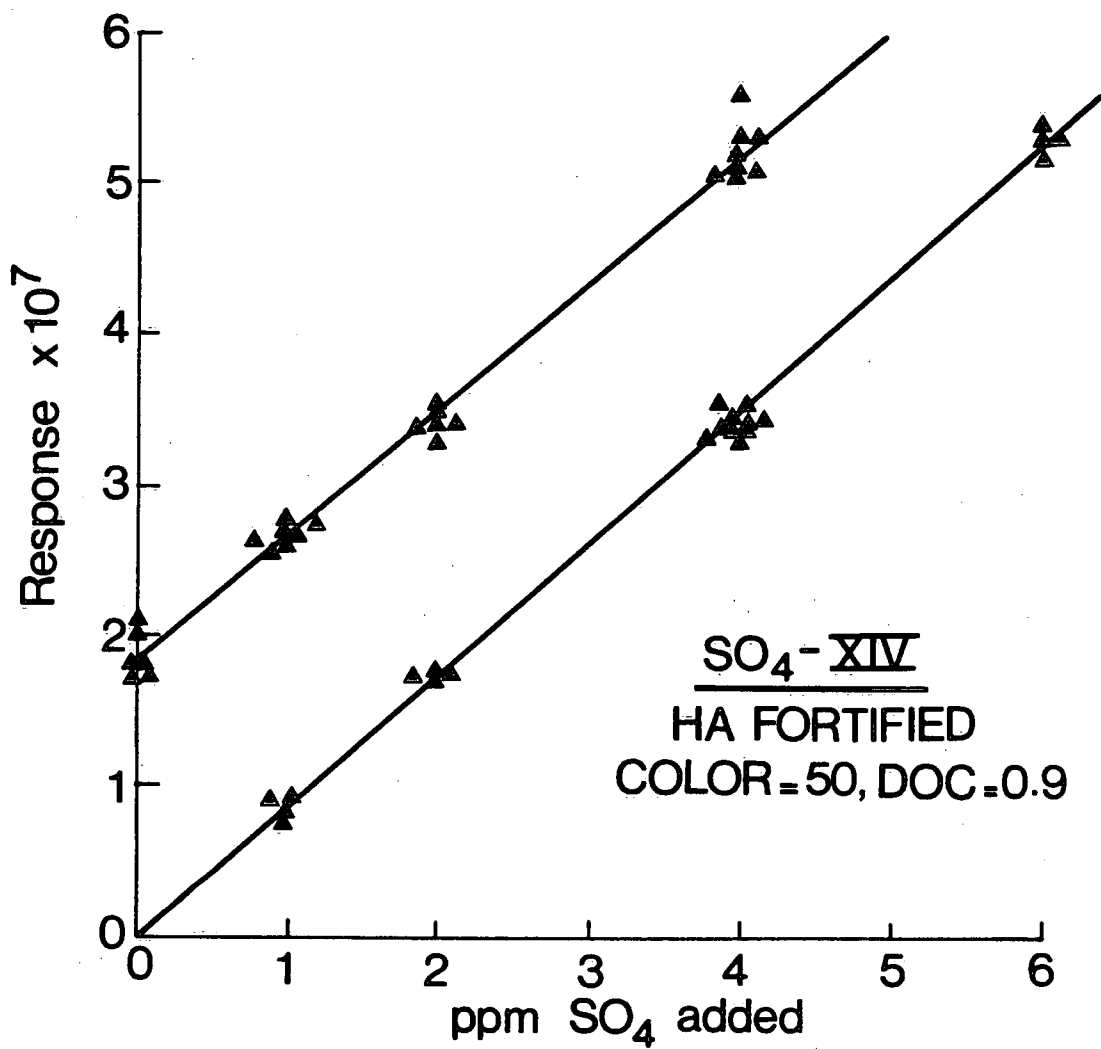
Fig. 10 IC STANDARD ADDITION CURVE FOR SO_4-XIV
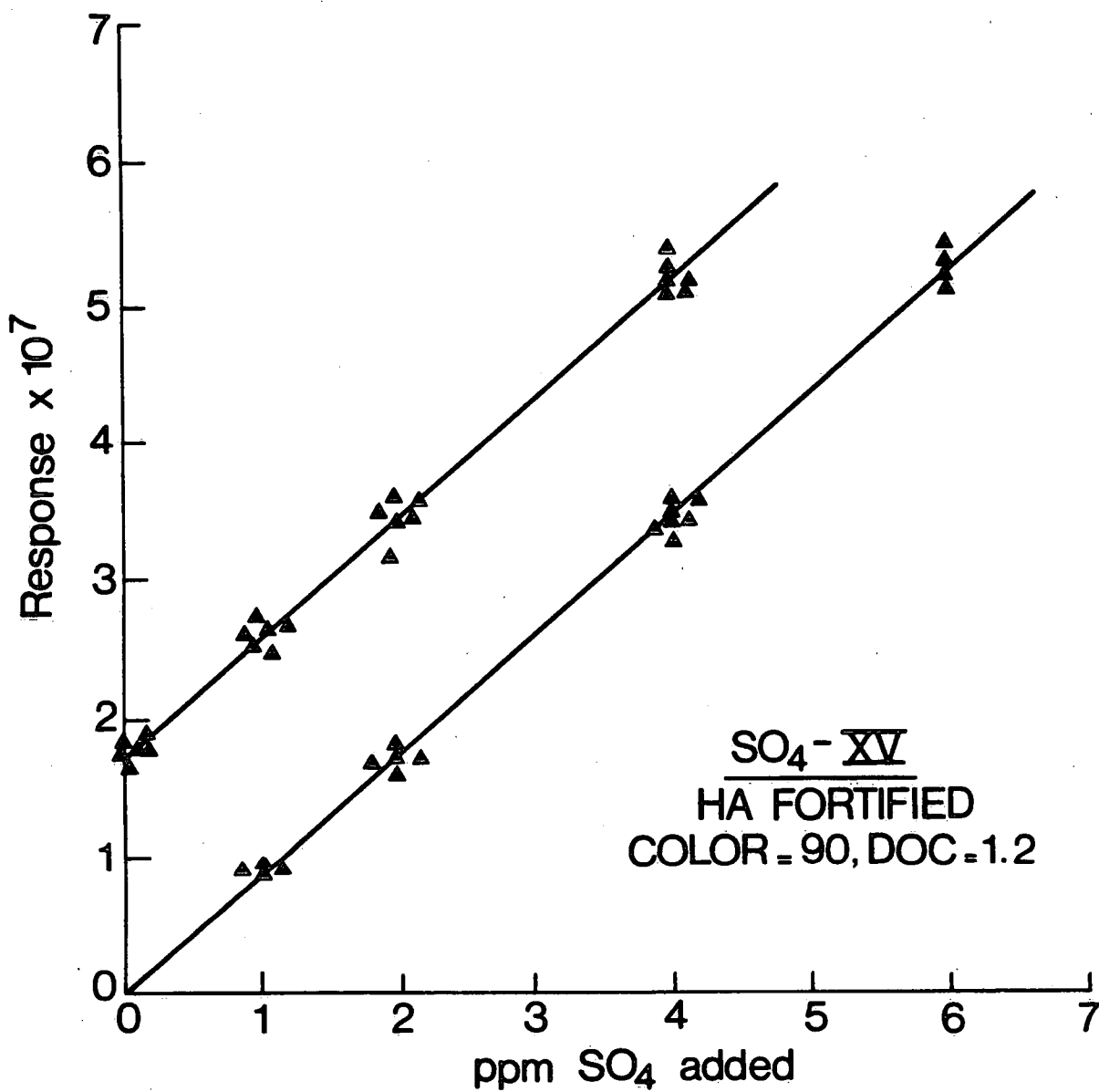
Fig. 11   IC STANDARD ADDITION CURVE FOR SO$_4$-XV
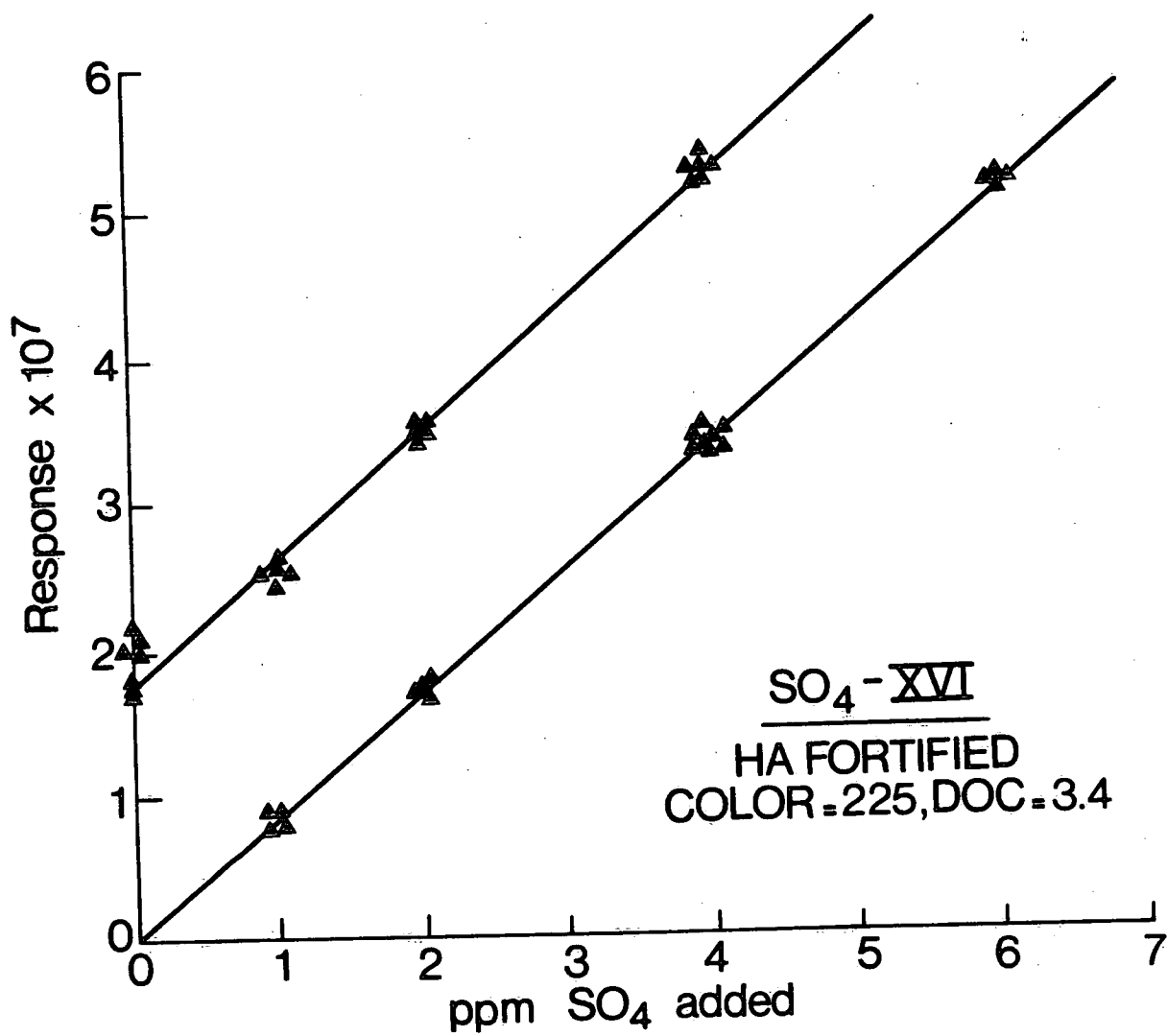
Fig. 12 IC STANDARD ADDITION CURVE FOR SO$_4$-XVI
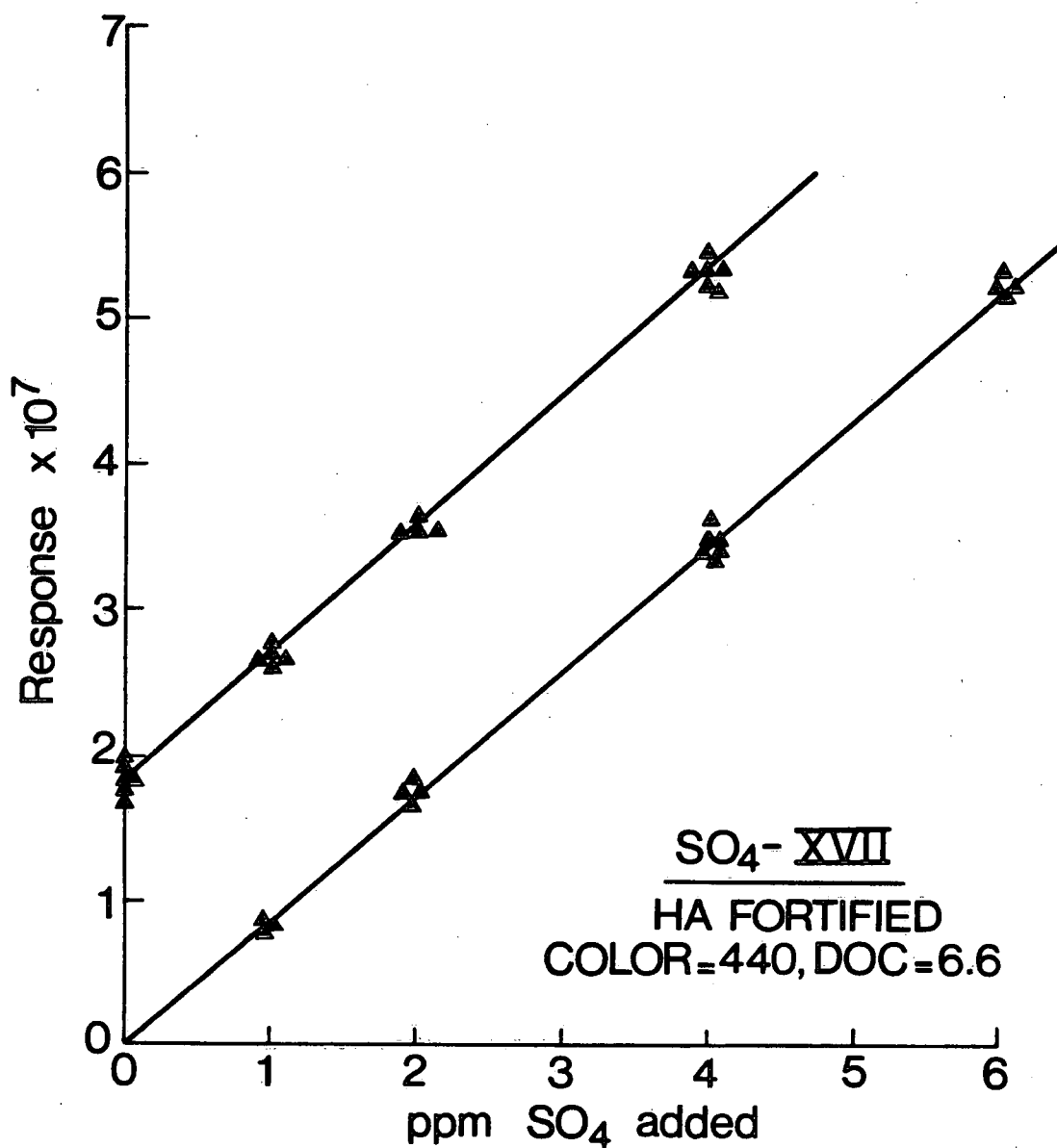
Fig. 13 IC STANDARD ADDITION CURVE FOR SO$_4$-XVII
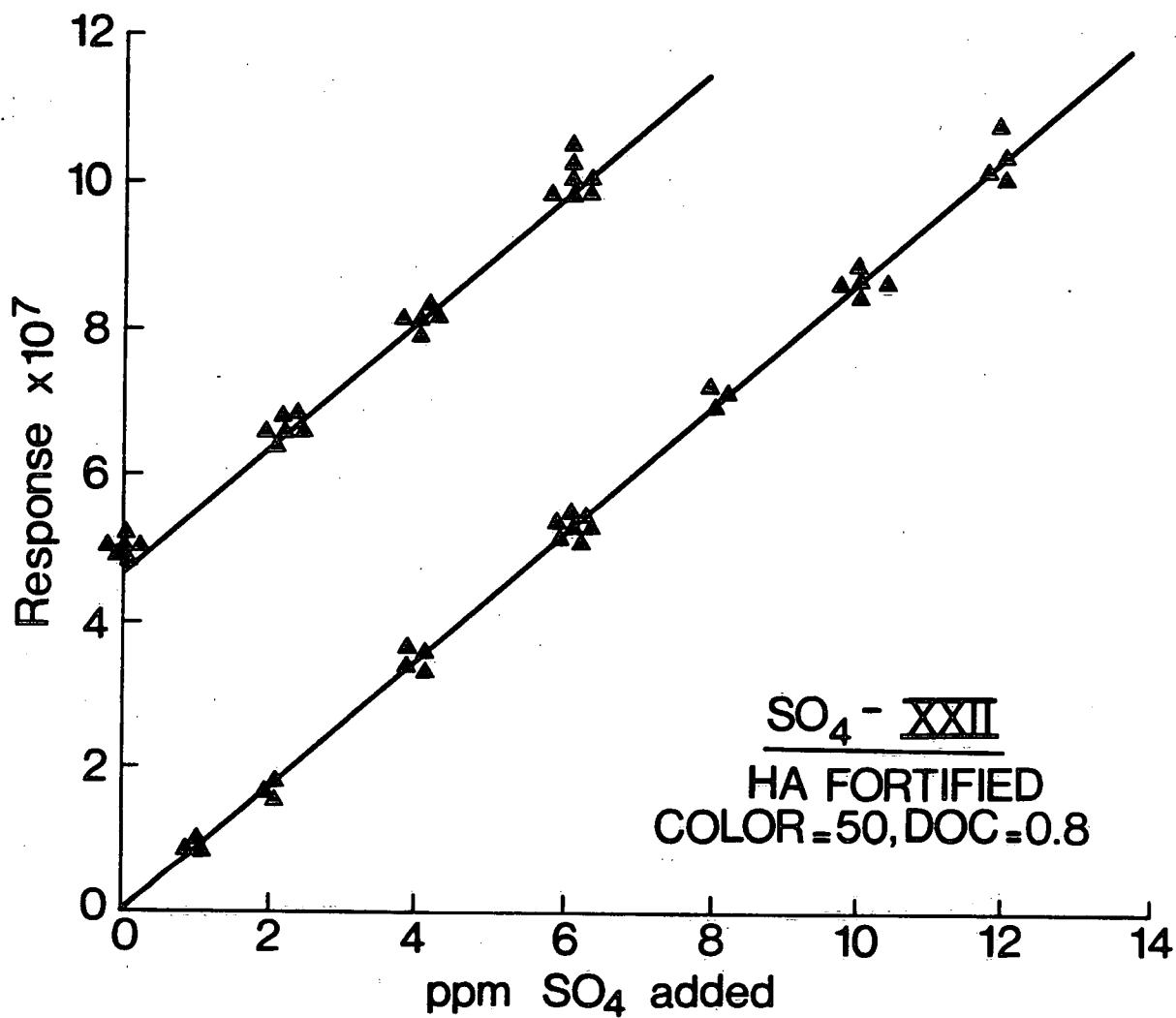
Fig. 14   IC STANDARD ADDITION CURVE FOR SO_4- XXII
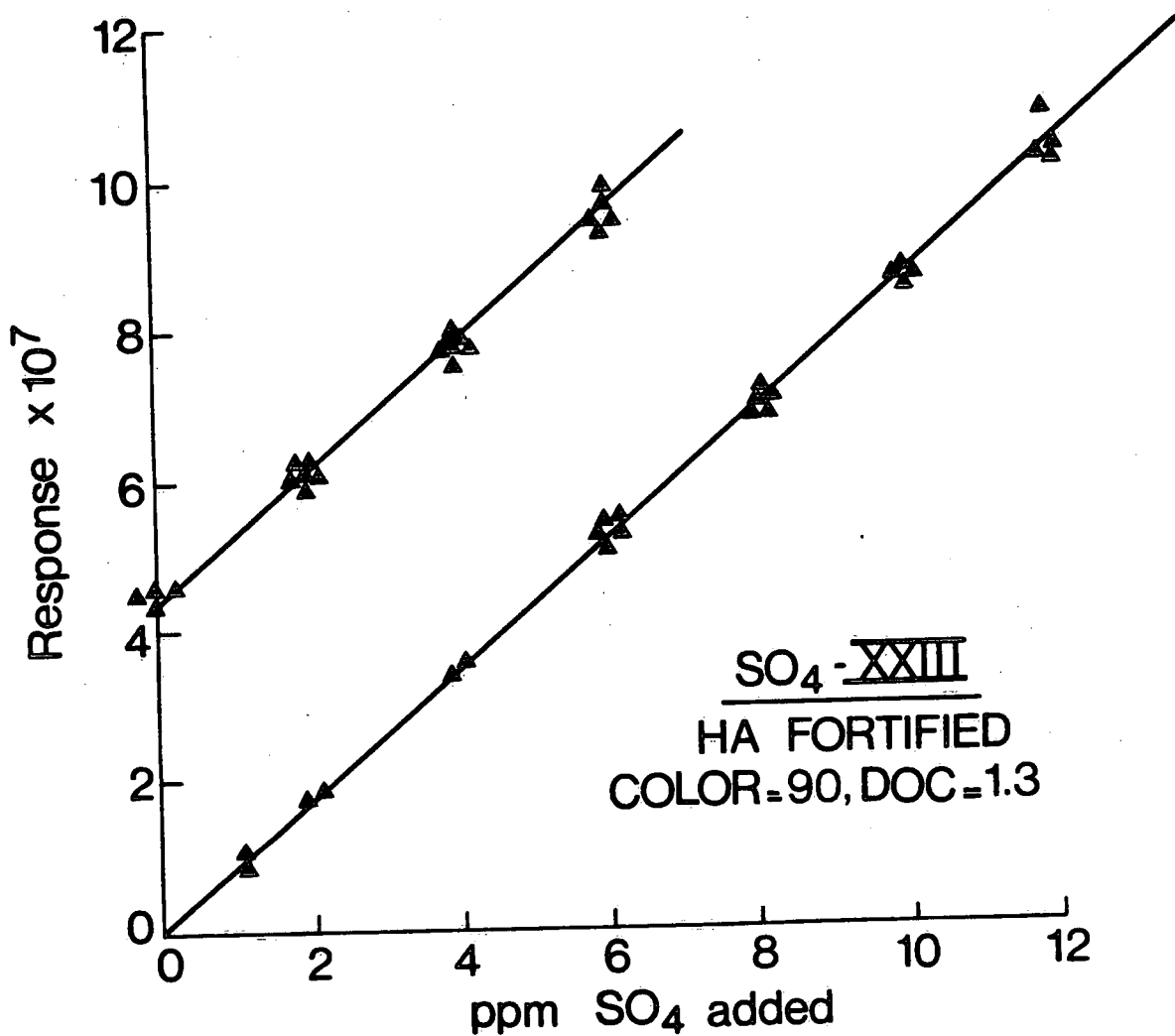
Fig. 15 IC STANDARD ADDITION CURVE FOR SO₄-XXIII
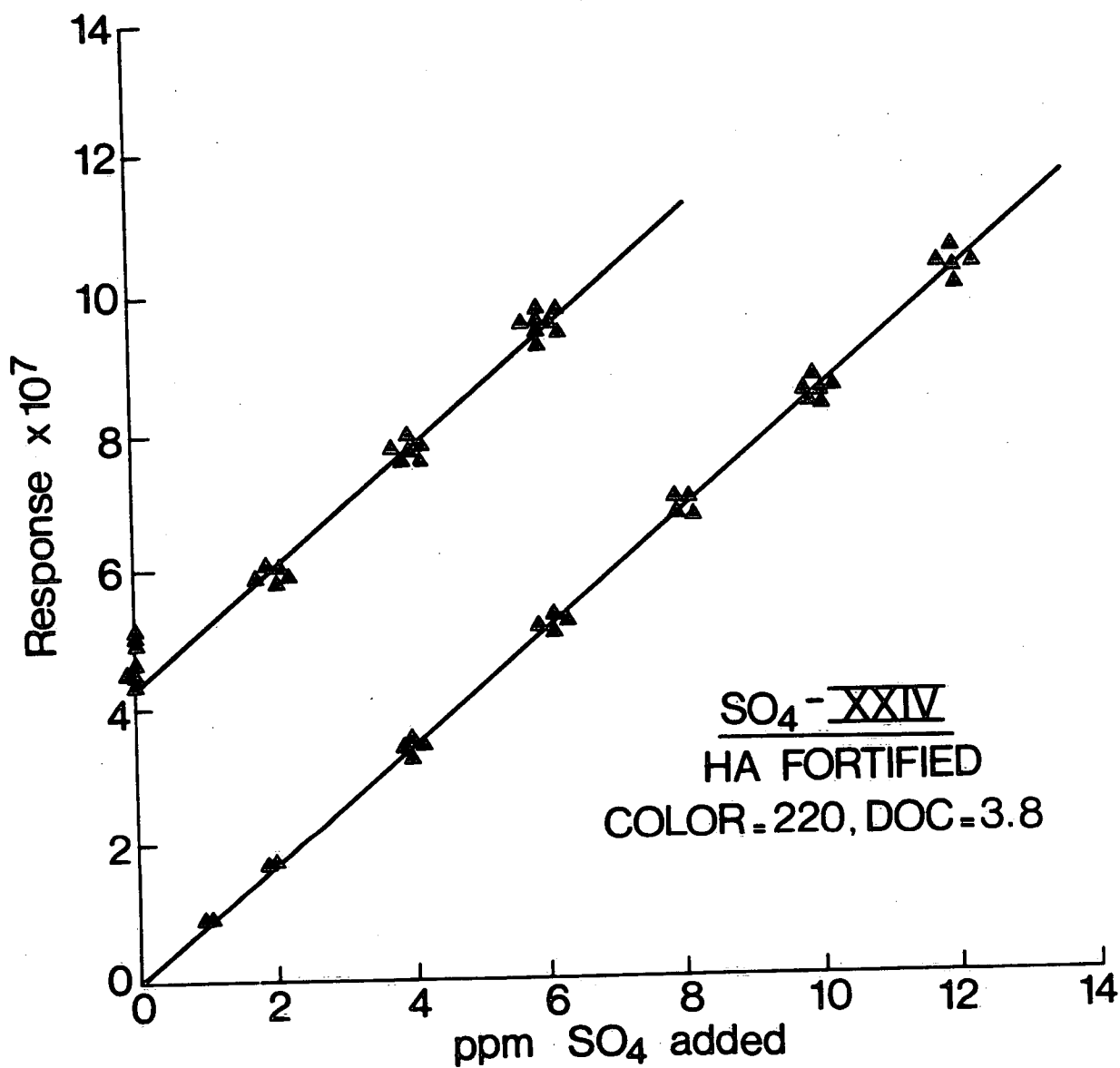
Fig. 16 IC STANDARD ADDITION CURVE FOR SO₄-XXIV
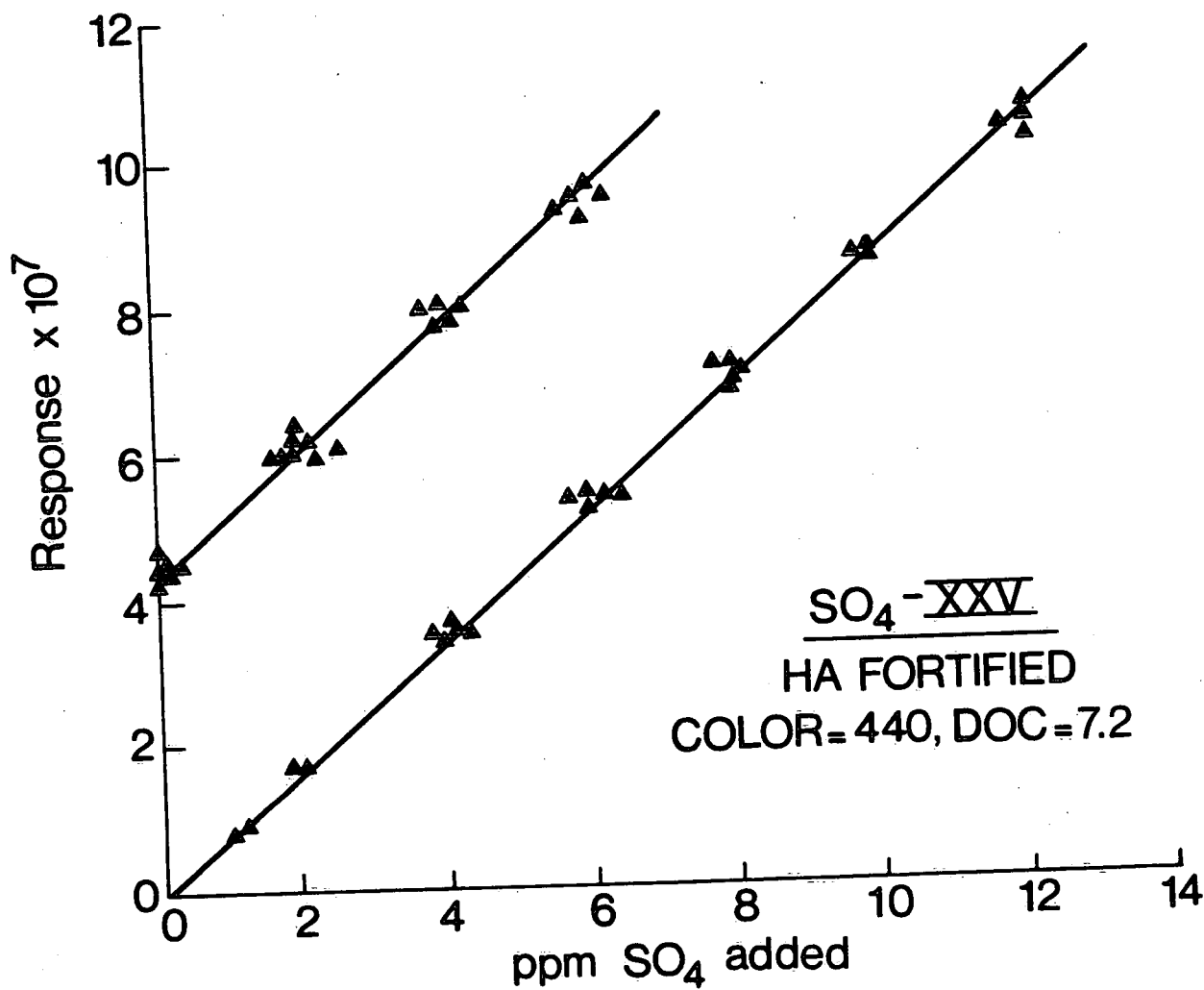
Fig. 17   IC STANDARD ADDITION CURVE FOR SO$_4$-XXV
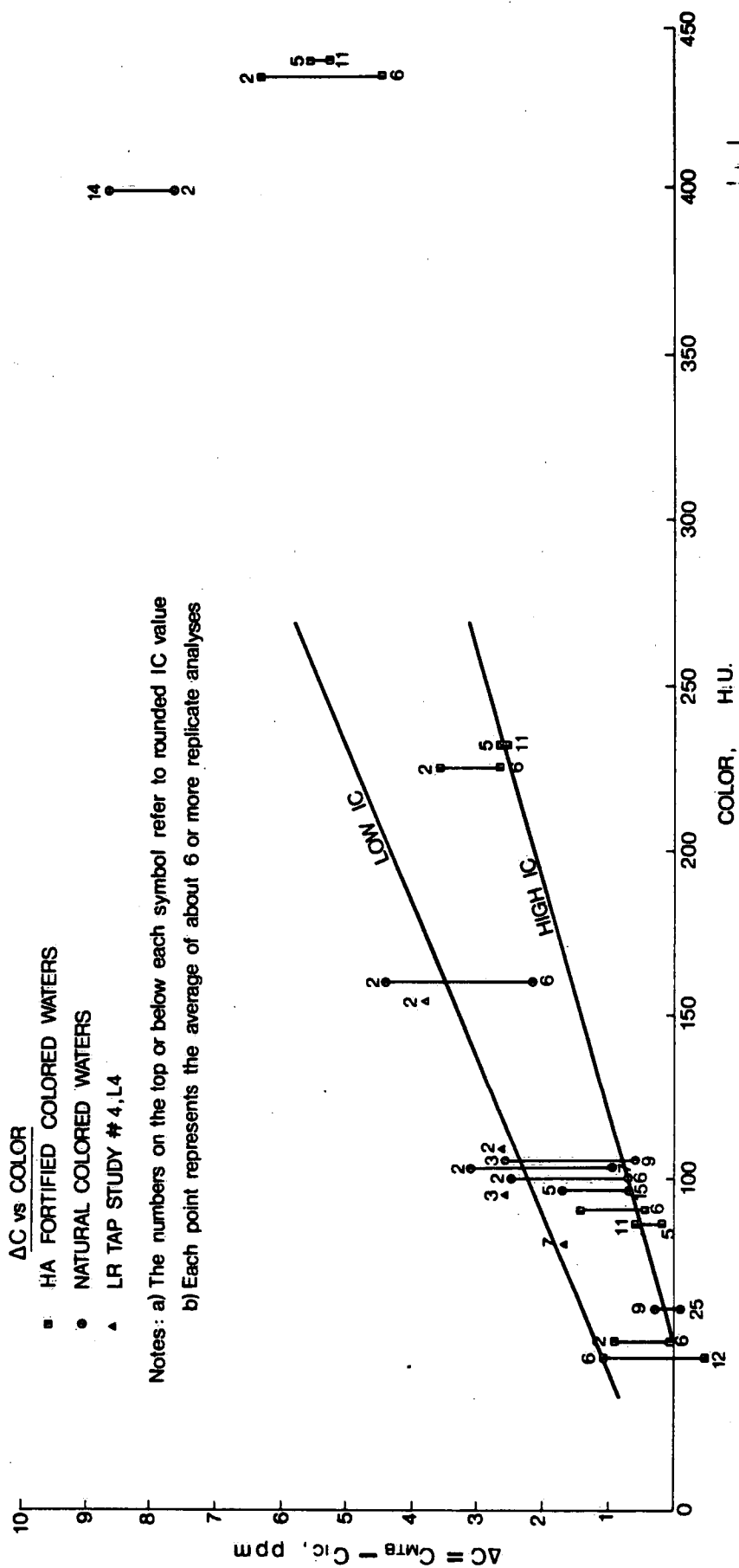
Fig. 18 RELATIONSHIP OF ΔC AND COLOR
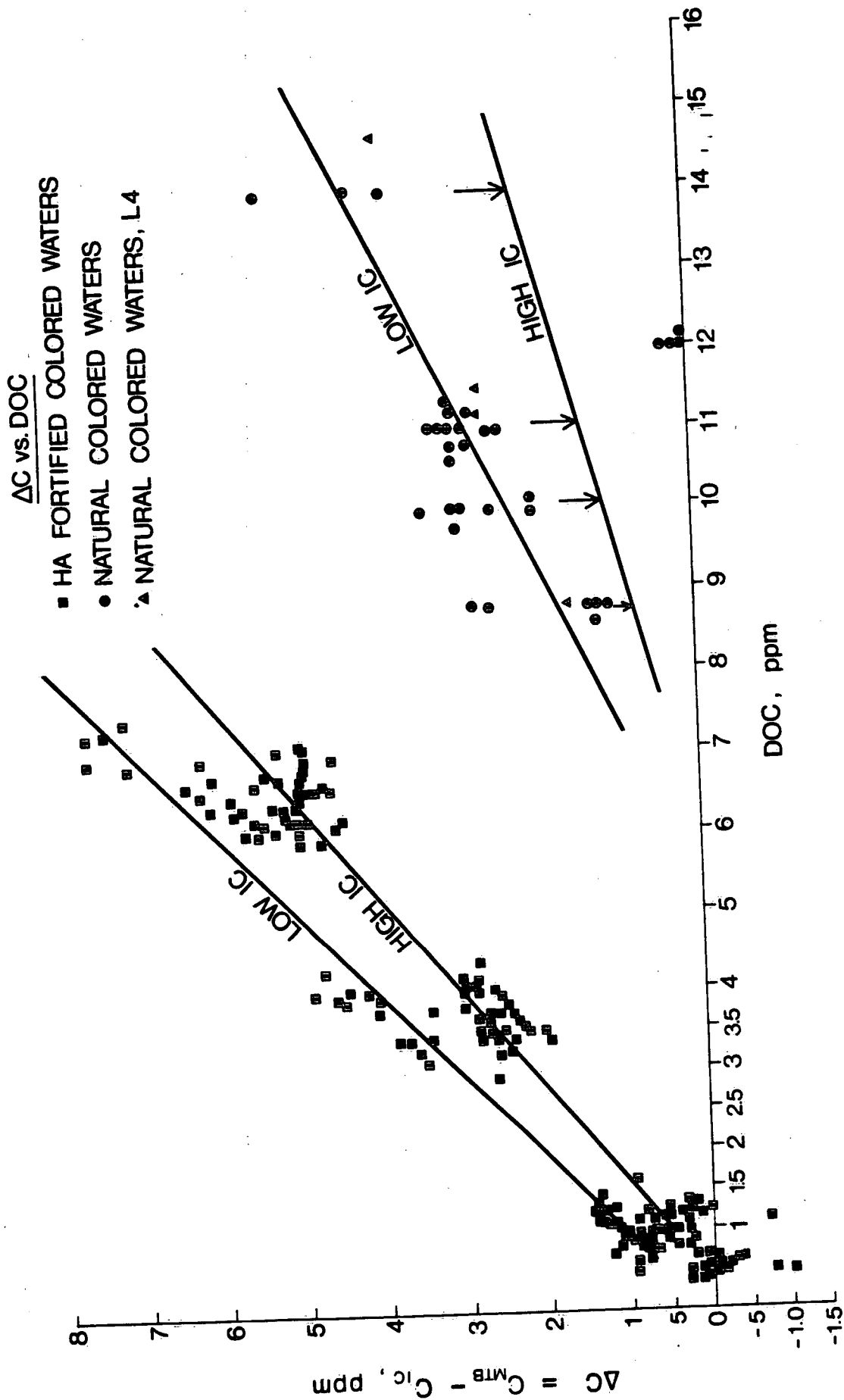
Fig. 19 RELATIONSHIP OF ΔC AND DOC
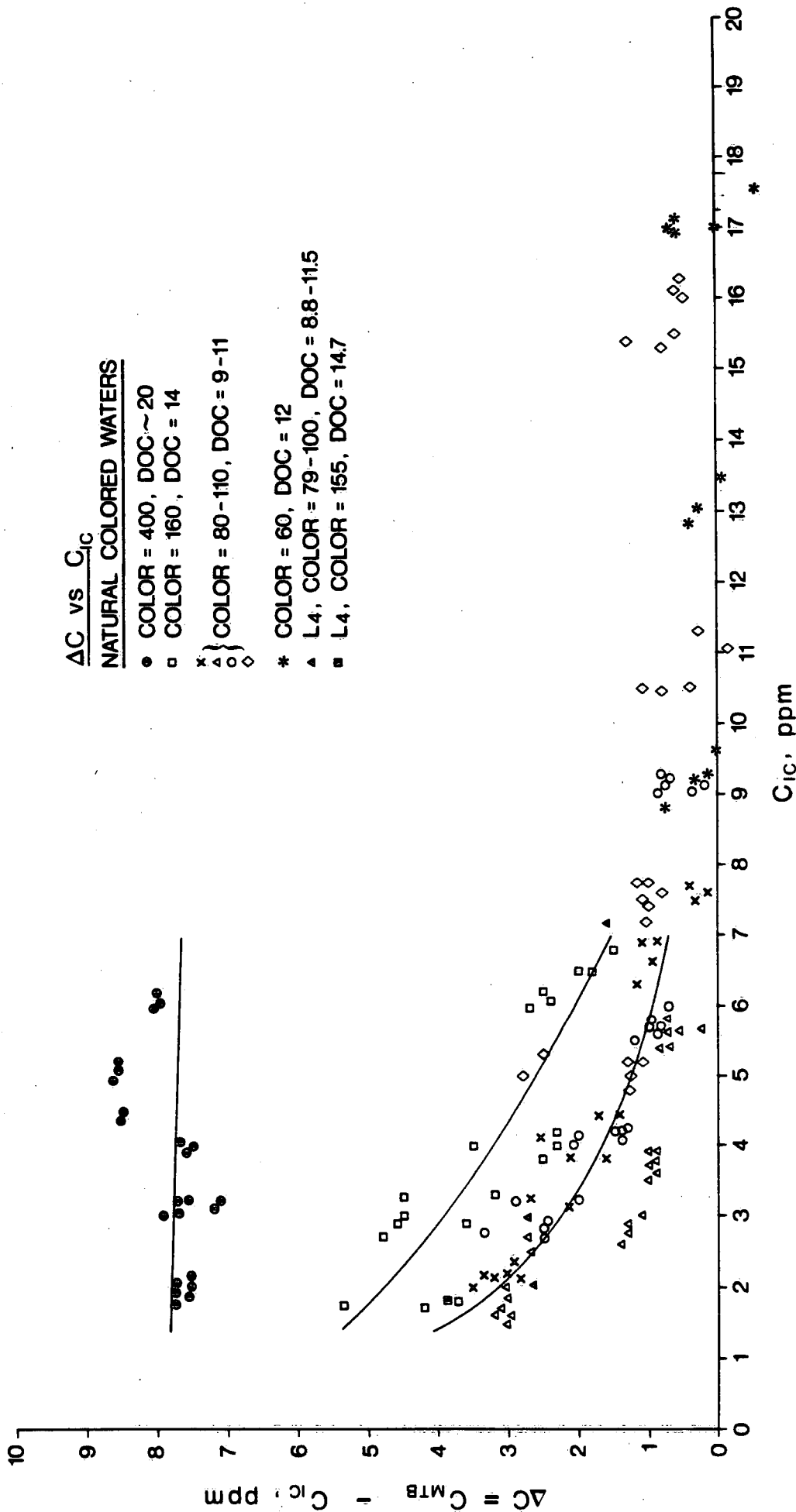
Fig. 20 RELATIONSHIP OF ΔC AND C_{ic} FOR NATURAL COLORED WATERS
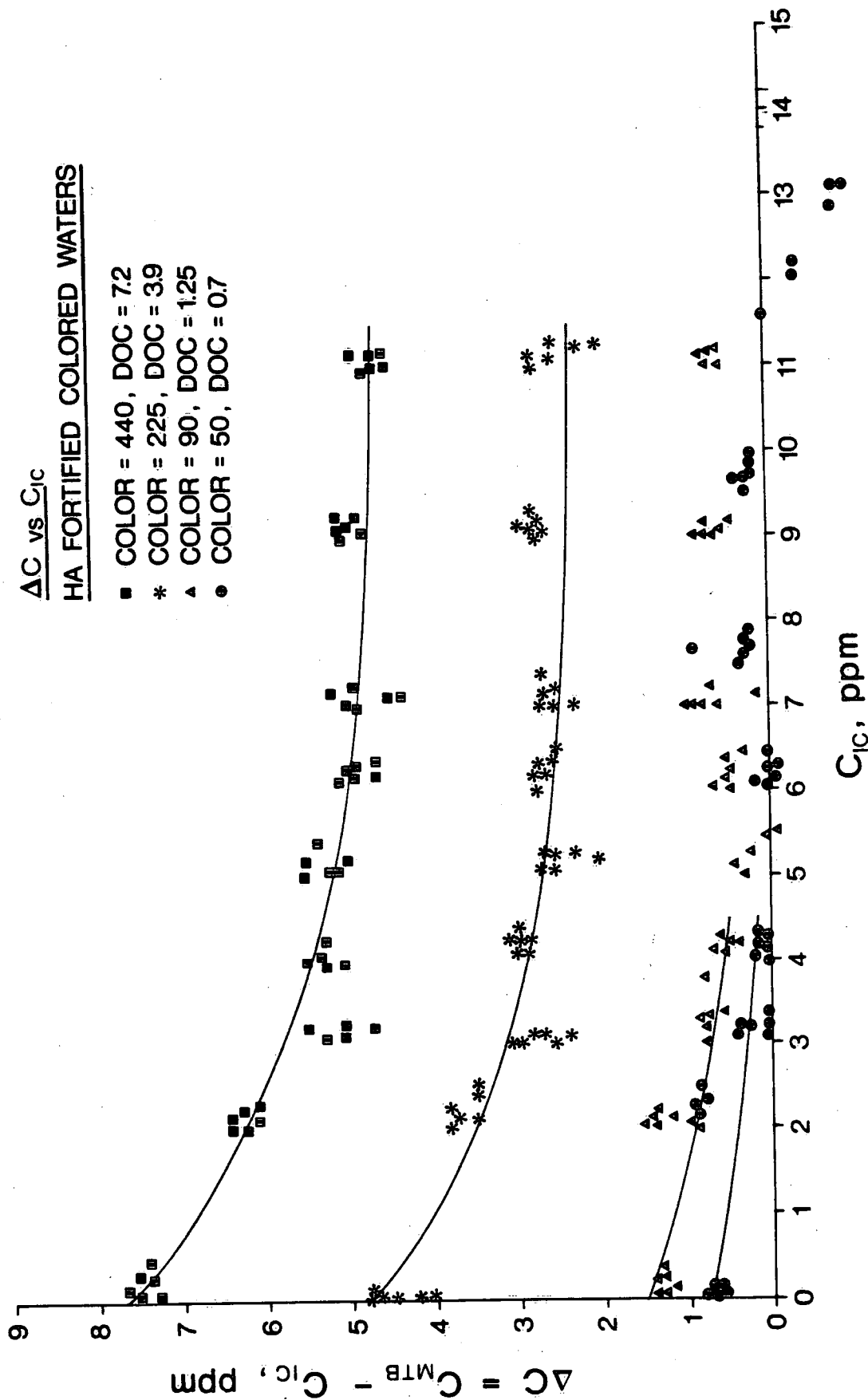
Fig. 21 RELATIONSHIP OF ΔC AND C_{IC} FOR HUMIC ACID FORTIFIED COLORED WATERS
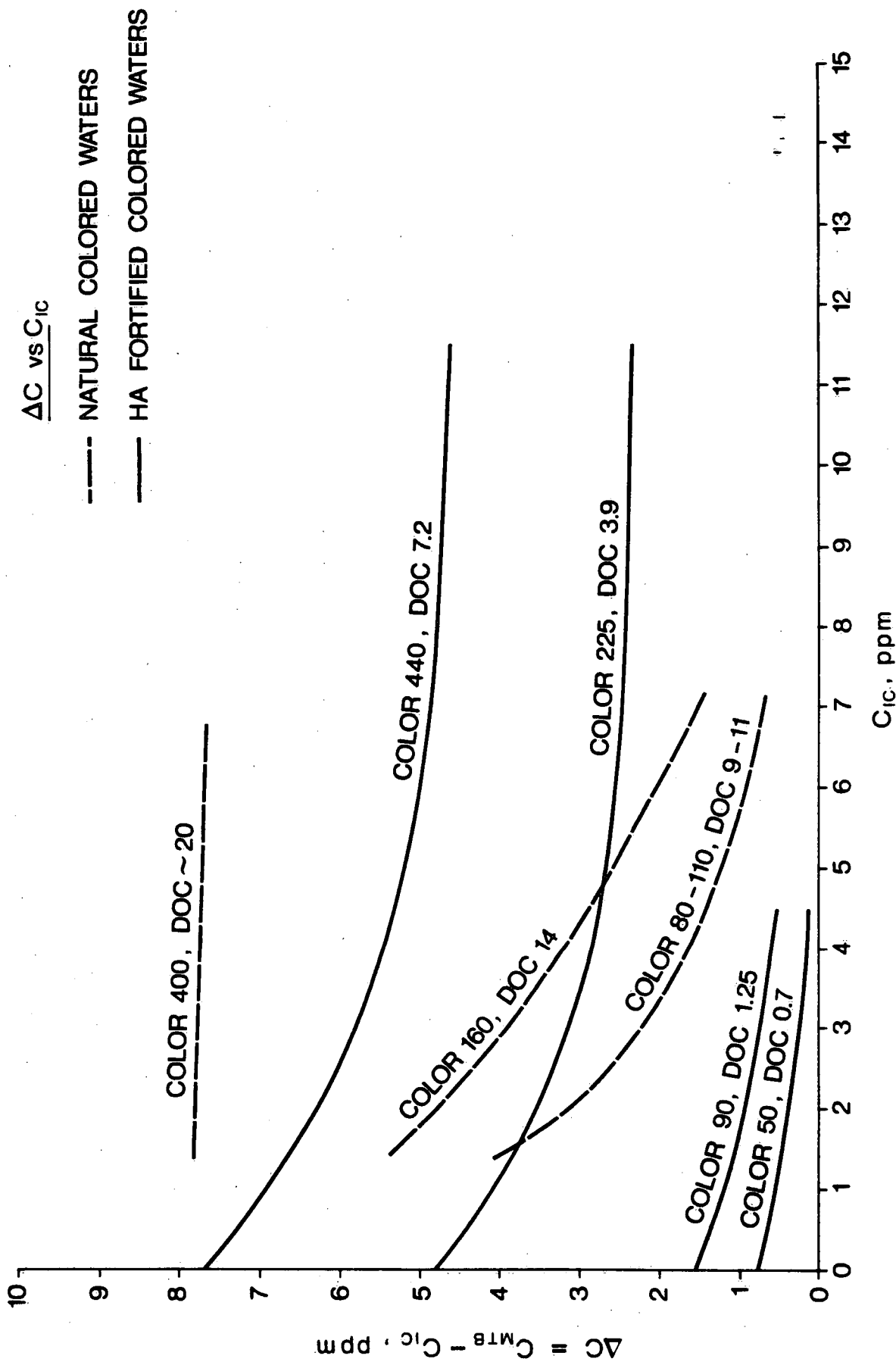
Fig. 22 RELATIONSHIP OF ΔC AND C_{IC} IN BOTH NATURAL AND HUMIC
ACID FORTIFIED COLORED WATERS
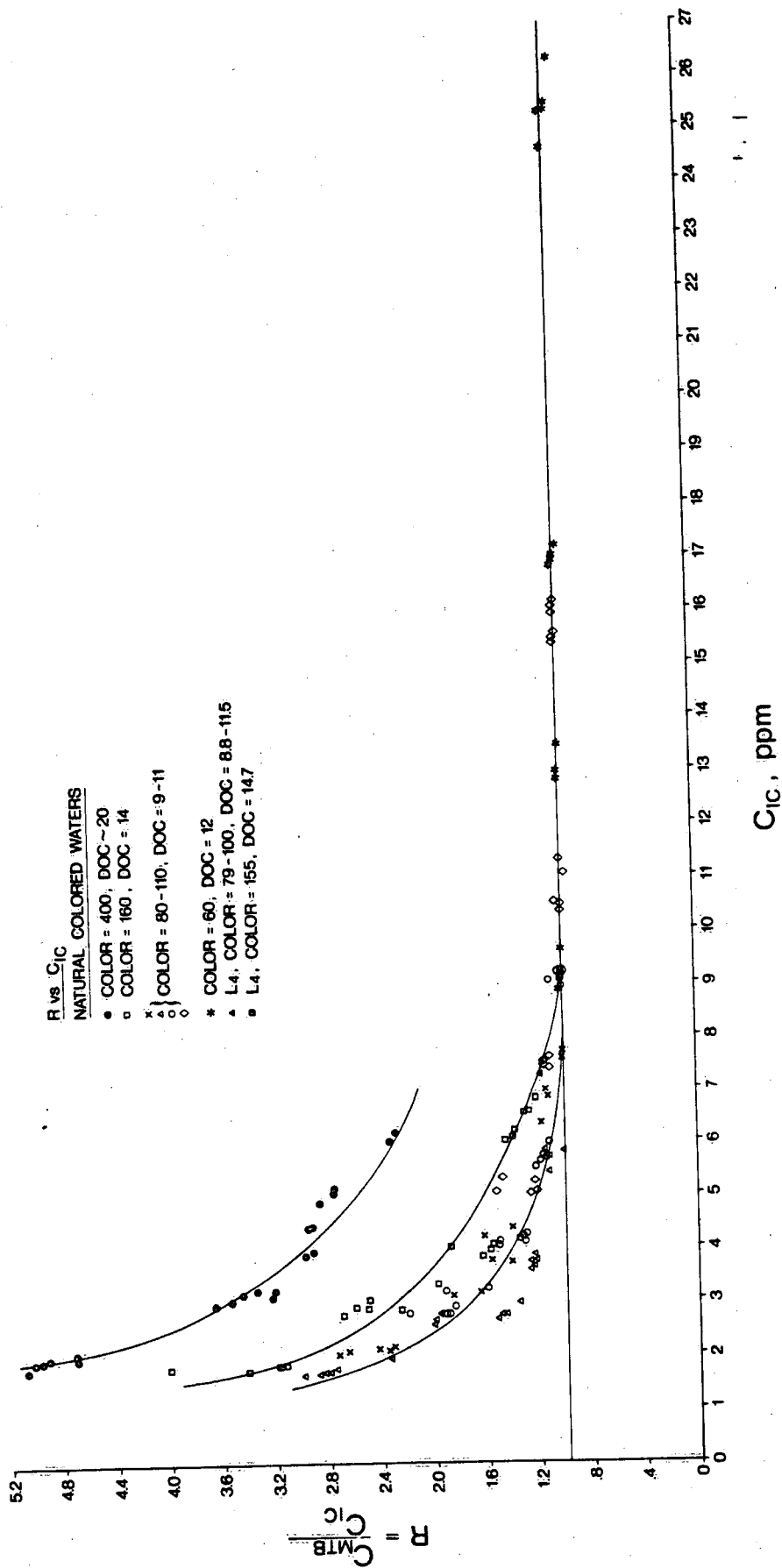
Fig. 23 RELATIONSHIP OF SO$_4$ RATIO, R, AND C$_{IC}$ FOR NATURAL COLORED WATERS
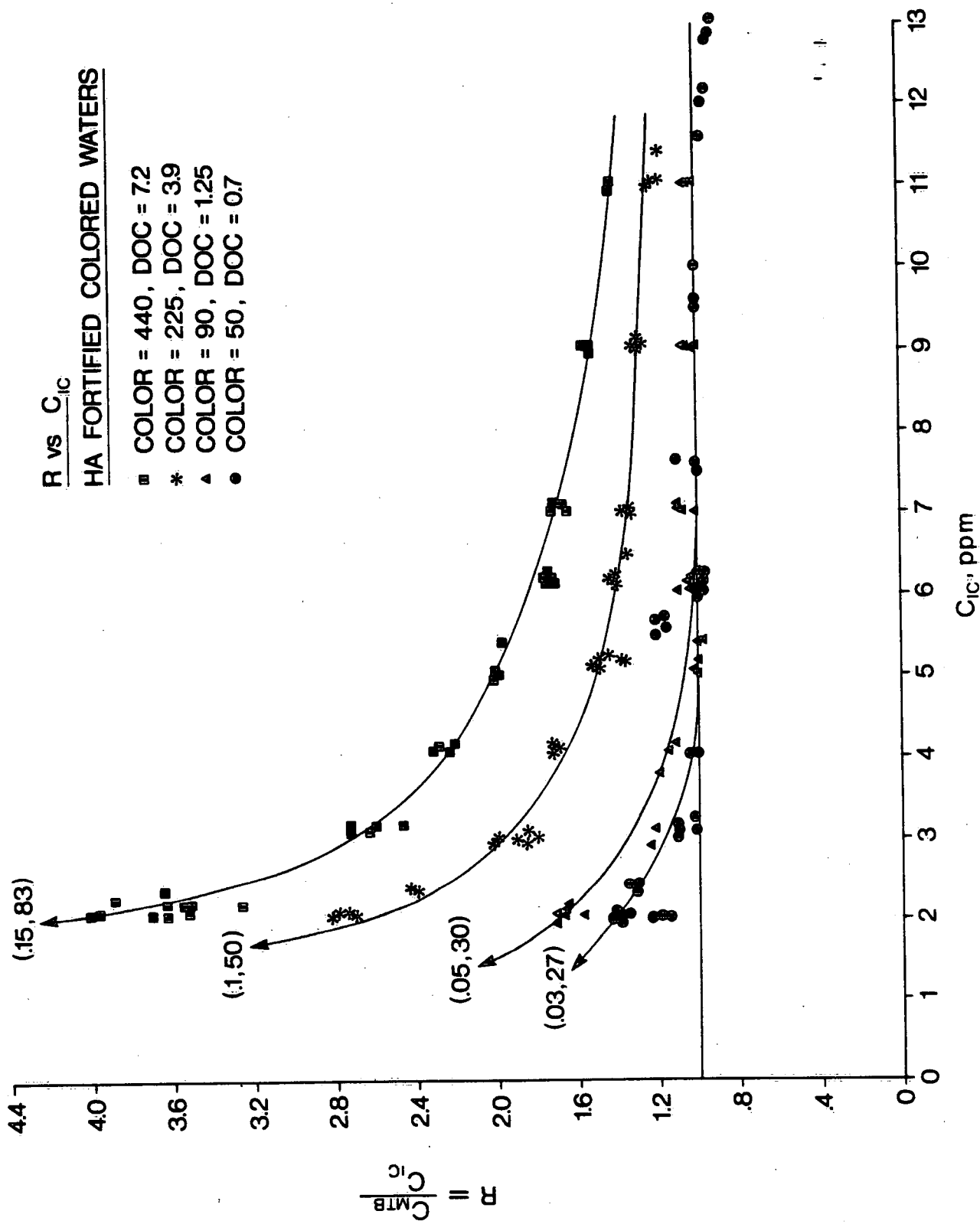
Fig. 24   RELATIONSHIP OF SO_4 RATIO, R, AND C_{ic} FOR HUMIC
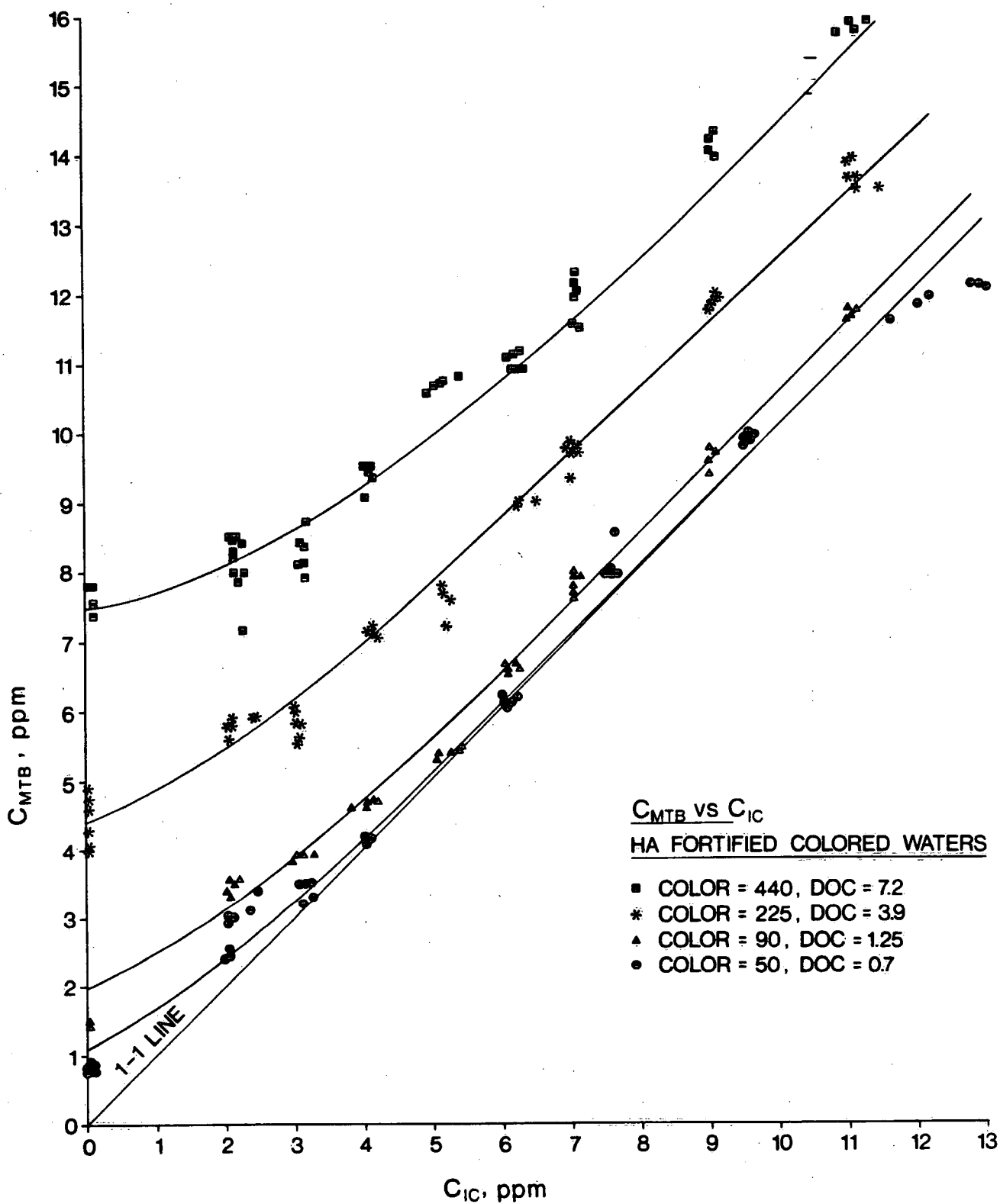ACID FORTIFIED COLORED WATERS

Fig. 25 THE $C_{MTB}-C_{IC}$ RELATIONSHIP FOR HUMIC
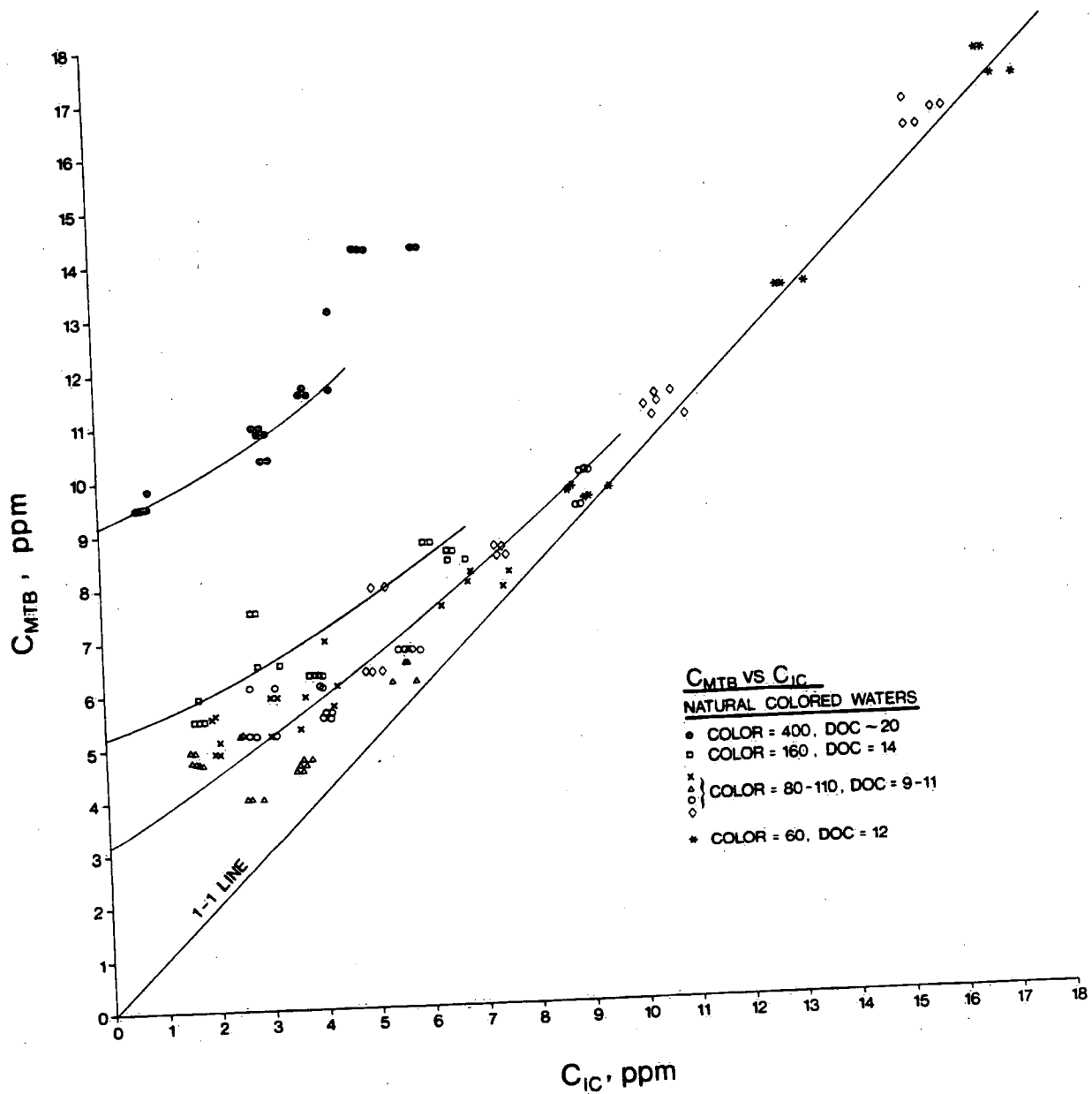ACID FORTIFIED COLORED WATERS

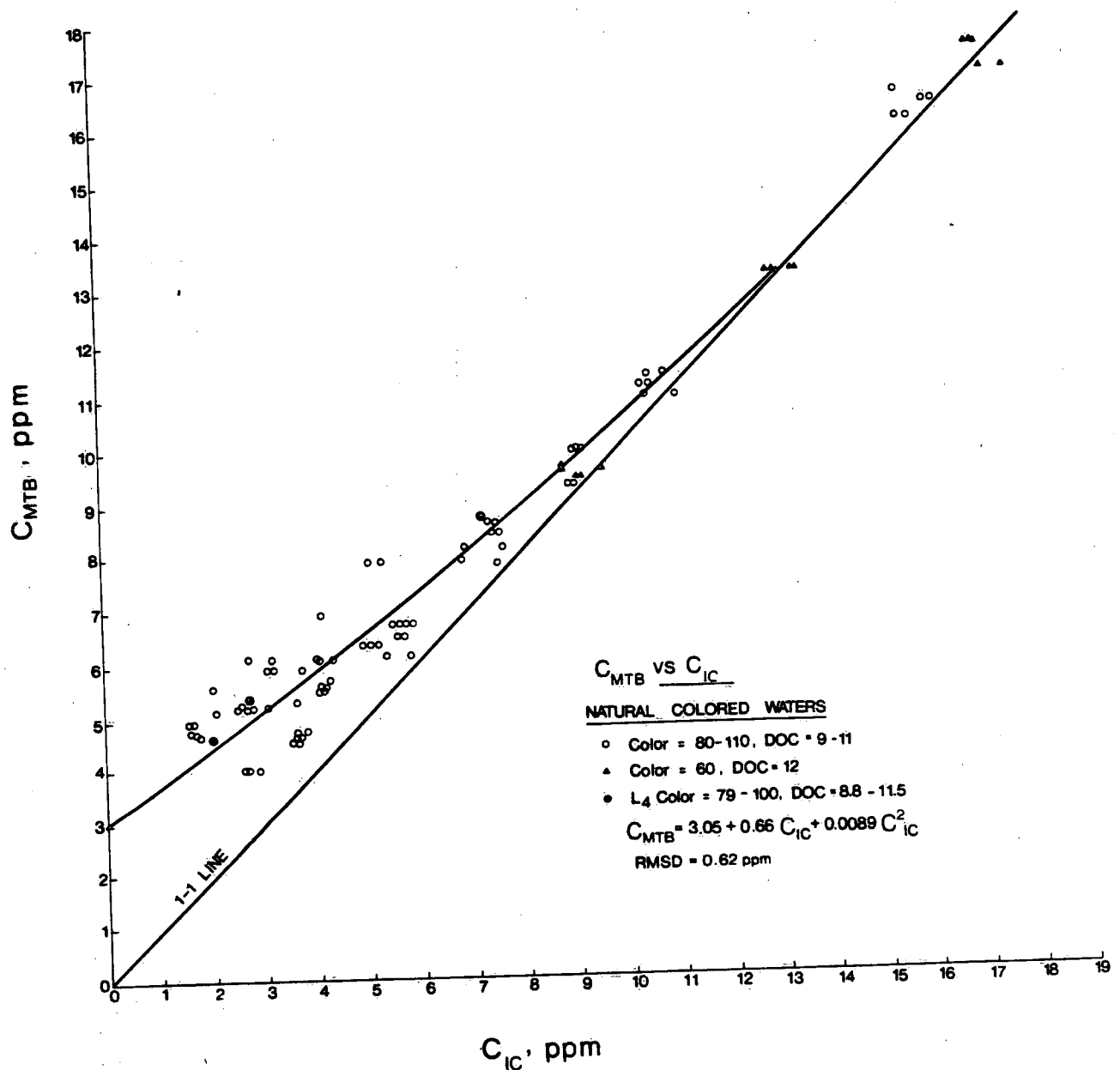Fig. 26 THE $C_{MTB} - C_{IC}$ RELATIONSHIP FOR NATURAL COLORED WATERS

Fig. 27 RELATIONSHIP OF C_{MTB} AND C_{IC} FOR THE FOUR NATURAL COLORED WATERS WITH COLOR 80-110 H.U. AND D.O.C. = 9-11 P.P.M.