

CHEAM

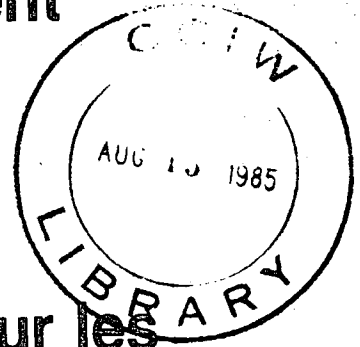


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FINAL SUMMARY REPORT

NATIONAL Q.C. STUDY NO. 33

V. CHEAM, A.S.Y. CHAU

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**FINAL SUMMARY REPORT
NATIONAL INTERLABORATORY QUALITY
CONTROL STUDY NO. 33
SULFATE IN COLOURED WATERS**

by

V. Cheam and A.S.Y. Chau

Quality Assurance and Methods Section

Analytical Methods Division

National Water Research Institute

Canada Centre for Inland Waters

Burlington, Ontario

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MANAGEMENT PERSPECTIVE

This study was carried out in conjunction with a recent sulfate project on validation of methodologies for analysis in coloured waters, requested by the WQB, Headquarters. It gives the WQ laboratories an opportunity to assess their data and methods against those of numerous other organizations across the country.

The study confirms that the colorimetric sulfate results in coloured waters are biased high and that ion chromatography is the method of choice for this type of analysis. It also shows that some laboratories, though using validated methods, do need to reevaluate their quality control practices, while some other laboratories perform very well. This study provides an excellent opportunity to the participants to find out how their laboratories fare among many others, which they wouldn't otherwise know from their in-house quality control alone.

BACKGROUND

This study was initiated in early December 1984, when we invited the participants of the National Q.C. Program to participate in the study.

In early February 1985, five coloured water samples were distributed to 60 laboratories, 54 of which provided analytical data. Several preliminary data summaries were sent out to participants for data confirmation. The final deadline of the study was set for April 12, 1985, and the final data summary was distributed in early May.

This summary report presents key graphical illustrations for determining laboratory and method performances. The study will be published in the IWD report series as customarily practiced.

DESCRIPTION OF TEST SAMPLES

The test samples used in this study were natural and spiked samples. We requested the participants to store the samples at 4°C to ensure sample integrity until analysis as there was no preservative added.

<u>Test Sample</u>	<u>Type</u>
1	Spiked sample
2	Mixture of coloured samples
3	Natural sample (Sand Pond)
4	Spiked sample
5	Spiked sample

RESULTS

Table 1 presents the interlaboratory results by Ion Chromatography (IC) method along with their mean, standard deviation and median values. Tables 2-7 present similar data by the following methods: Methyl Thymol Blue, MTB (Table 2), Calmagite (Table 3), turbidimetry (Table 4), gravimetry (Table 5), titration using Thorin as indicator (Table 6), and other methods (Table 7). These other methods include MTB (with colour correction and sample digestion using UV/H₂O₂ procedure) and Inductively Coupled Argon Plasma (ICAP).

Samples 1, 2, 4 and 5 have similar background matrix. All the results from each of these samples are graphically presented as paired sample plots¹ in Figures 1 to 3. It can be seen that the MTB results generally cluster at the upper right hand corner with respect to IC results, which cluster around the design values. The latter values are estimated from the many in-house analyses and the spiked

amounts, and are supported by the findings of a previous study² and by several investigations on colour and organic carbon removal.

Laboratory performance is determined by the distance from the design value. The closer a laboratory is to the design value, the better its performance (Figures 1-3). The design value for sample 3 is 2.4 ppm SO₄.

To compare the performance of the various methodologies, we plotted the median results from each method along with the corresponding design values in Figures 4-6. The figures clearly indicate that the conventional MTB method produces biased high results.

The above illustrations permit each participant to easily determine how his/her laboratory and method perform in the study.

ACKNOWLEDGEMENTS

The managers and analysts of laboratories who participated and provided their data are gratefully acknowledged.

REFERENCES

1. Youden, W.J. 1959. Industrial Quality Control. 15:24.
2. Cheam, V., A.S.Y. Chau and S. Todd. NWRI Contribution No. 85-95.

TABLE 1 RESULTS BY METHOD

NAT33 NATIONAL INTERLAB STUDY NO.33 (SO₄ IN WATER)

PRINTOUT PREPARED: 85/05/15.

PARAMETER: SULFATE, IC METHOD

MG /L

SAMPLE RESULTS

	1	2	3	4	5
LAB					
N002	4.45	2.8	2.3	5.85	9.2
N003	4.25	2.91	2.47	5.48	7.76
N004	4.36	3.19	2.45	6.07	8.97
N005	4.55	2.85	2.44	6.19	9.04
N010	4.21	2.70	2.05	5.65	8.77
N012	4.48	2.92	2.42	5.34	9.25
N015	4.2	2.7	2.25	5.6	8.9
N018	4.81	3.23	3.05	6.443	9.71
N019	4.3	2.7	2.4	5.7	8.5
N023	2.8	4.1	2.4	5.6	8.58
N034	4.27	2.89	2.48	5.73	8.78
N047	4.2	2.9	3.3	5.9	9.0
N051B	4.3	3.1	2.5	6.1	8.7
N058	6.3	3.4	3.0	6.1	8.9
N060	4.39	2.78	2.35	5.68	8.77
N064	4.0	2.6	2.2	5.4	8.3
N070	3.99	2.80	2.44	5.54	8.20
N072	4.0	2.65	2.5	5.45	8.50
N074	4.1	2.8	2.8	5.4	8.3
N085	3.8	3.1	2.5	29.0	8.7
N089	4.34	2.72	2.33	5.61	8.50
N090	4.03	2.62	2.2	5.61	8.25
N096	4.42	2.75	2.54	6.23	9.28
N100B	8.6	3.7	2.5	6.5	8.9
N105	5.14	2.66	2.24	5.74	8.52
N124	5.53	4.08	3.00	6.84	8.70
N125	4.34	2.83	2.41	5.81	8.80
N128	4.27	2.79	2.33	5.87	8.97
N130	4.44	2.94	2.53	5.37	9.76
N131	4.2	2.7	2.1	5.6	8.7
N132	4.55	2.95	2.5	6.95	9.15
TOTAL LABS REPORTING	31	31	31	31	31
TOTAL LABS USED	31	31	31	31	31
MEAN	4.50387	2.96516	2.47419	6.64365	8.76742
STD DEV	.94587	.38639	.28467	4.16848	.44277
MEDIAN	4.30000	2.83000	2.44000	5.81000	8.77000

TABLE 2 RESULTS BY MB METHOD

NAT 33 NATIONAL INTERLAB STUDY NO.33 (SO4 IN WATER)

PRINTOUT PREPARED: 85/05/15.

PARAMETER: SULPHATE, MB METHOD

MG SO4/L

SAMPLE RESULTS

	1	2	3	4	5
LAB					
N002B	6.5	4.6	5.4	7.1	10.0
N003B	6.8	5.6	7.1	8.2	11.8
N004B	6.6	5.3	6.4	8.1	10.8
N005B	6.6	4.2	4.4	6.9	9.7
N008	5.0	3.9	4.4	5.1	7.6
N010B	6.15	5.19	6.40	8.10	10.3
N012	6.39	4.55	5.60	8.24	11.7
N013	8.	7.	9.	10.	13.
N019	7.4	5.6	7.4	8.5	11.5
N048	3.7	6.4	8.2	9.7	12.6
N052	6.6	5.6	7.1	8.5	9.5
N070B	7.5	6.5	8.0	9.5	12.0
N100	6.7	5.6	7.6	8.1	10.
N106	7.92	5.46	6.94	8.37	11.00
N110	6.27	5.33	7.0	6.63	9.93
N112	10.8	8.0	9.6	9.6	14.8
N120	7.6	6.2	7.8	8.7	11.4
TOTAL LABS REPORTING	17	17	17	17	17
TOTAL LABS USED	17	17	17	17	17
MEAN	6.85471	5.59000	6.96118	8.19647	11.00059
STD DEV	1.45935	1.02565	1.43871	1.24009	1.61269
MEDIAN	6.60000	5.60000	7.10000	8.24000	11.00000

TABLE 3 RESULTS CALMAGITE METHOD

NAT33 NATIONAL INTERLAB STUDY NO.33 (SO4 IN WATER)

PRINTOUT PREPARED: 85/05/15.

PARAMETER: SULPHATE, CALMAGNITE MG SO4/L

	SAMPLE RESULTS				
	1	2	3	4	5
LAB N051	4.0	2.4	1.8	5.4	8.4
TOTAL LABS REPORTING	1	1	1	1	1
TOTAL LABS USED	1	1	1	1	1
MEAN	4.00000	2.40000	1.80000	5.40000	8.40000
STD DEV	0.00000	0.00000	0.00000	0.00000	0.00000
MEDIAN	4.00000	2.40000	1.80000	5.40000	8.40000

TABLE 4 RESULTS BY TURBIDIMETRY METHOD
 NAT33 NATIONAL INTERLAB STUDY NO.33 (SO4 IN WATER)

PRINTOUT PREPARED: 85/05/15.

PARAMETER: SULPHATE, TURBIDIMETRIC MG SO4/L

LAB	SAMPLE RESULTS				
	1	2	3	4	5
N026	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
N030	5.0	4.0	5.0	6.0	8.0
N041	3.5	2.5	2.0	4.9	8.6
N043	4.5	3.4	2.8	5.9	9.0
N047	3.75	1.55	.4	5.5	7.75
N053	5.0	1.2	.9	5.6	7.9
N058B	6.1	3.8	2.2	6.1	9.1
N072B	3.	1.	1.	5.	9.5
N098	6.	4.	5.	7.	12.
N109	5.14	2.91	1.30	9.97	10.19
TOTAL LABS REPORTING	10	10	10	10	10
TOTAL LABS USED	9	9	9	9	9
MEAN	4.44333	2.70667	2.28889	6.21889	9.11556
STD DEV	1.19912	1.20552	1.70253	1.53987	1.34575
MEDIAN	4.50000	2.91000	2.00000	5.90000	9.00000

TABLE 5 RESULTS GRAVIMETRY METHOD

NAT33 NATIONAL INTERLAB STUDY NO.33 (SO4 IN WATER)

PRINTOUT PREPARED 85/05/15.

PARAMETER: SULPHATE, GRAVIMETRIC

MG SO4/L

SAMPLE RESULTS

	1	2	3	4	5
LAB					
N0158	7.	4.	5.	9.	13.
N029	81.9	2.1	1.6	3.3	7.4
N058C	4.1	4.9	4.9	11.5	19.7
N102	5.4	5.6	3.0	6.3	9.4
N1128	12.	8.	10.	10.	15.
N119	8.4	5.1	2.0	2.0	7.2
N135	2.	1.	4.	5.	6.
TOTAL LABS REPORTING	7	7	7	7	7
TOTAL LABS USED	7	7	6	6	7
MEAN	17.25714	4.38571	4.75000	7.51667	11.10000
STD DEV	28.68355	2.31476	2.87037	3.15684	5.00966
MEDIAN	7.00000	4.90000	4.45000	7.65000	9.40000

TABLE 6 RESULTS BY TITRATION METHOD
 NAT33 NATIONAL INTERLAB STUDY NO.33 (SO₄ IN WATER)

PRINTOUT PREPARED: 85/05/15.

PARAMETER: SULPHATE, THORIN TITRATION MG SO₄/L

	SAMPLE RESULTS				
	1	2	3	4	5
LAB					
N053B	4.	1.	2.	6.	10.
TOTAL LABS REPORTING	1	1	1	1	1
TOTAL LABS USED	1	1	1	1	1
MEAN	4.00000	1.00000	2.00000	6.00000	10.00000
STD DEV	0.00000	0.00000	0.00000	0.00000	0.00000
MEDIAN	4.00000	1.00000	2.00000	6.00000	10.00000

TABLE 7 RESULTS BY OTHER METHODS*

NAT33 NATIONAL INTERLAB STUDY NO.33 (SO4 IN WATER)

PRINTOUT PREPARED: 85705715.

PARAMETER: SULPHATE, OTHERS

MG SO4/L

LAB	SAMPLE RESULTS				
	1	2	3	4	5
N004C	4.8	3.5	3.6	6.1	8.7
N022	4.7	3.3	3.0	6.2	9.1
N025	5.34	3.79	3.36	6.45	9.84
TOTAL LABS REPORTING	3	3	3	3	3
TOTAL LABS USED	3	3	3	3	3
MEAN	4.94667	3.53000	3.32000	6.25000	9.21333
STD DEV	.34429	.24637	.30199	.18028	.57839
MEDIAN	4.80000	3.50000	3.36000	6.20000	9.10000

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* LAB 4 = color corrected results by MTB

LAB 22 = results on samples pretreated by UV/H₂O₂
followed by MTB analysis

LAB 25 = results by ICAP (Inductively coupled Argon plasma)

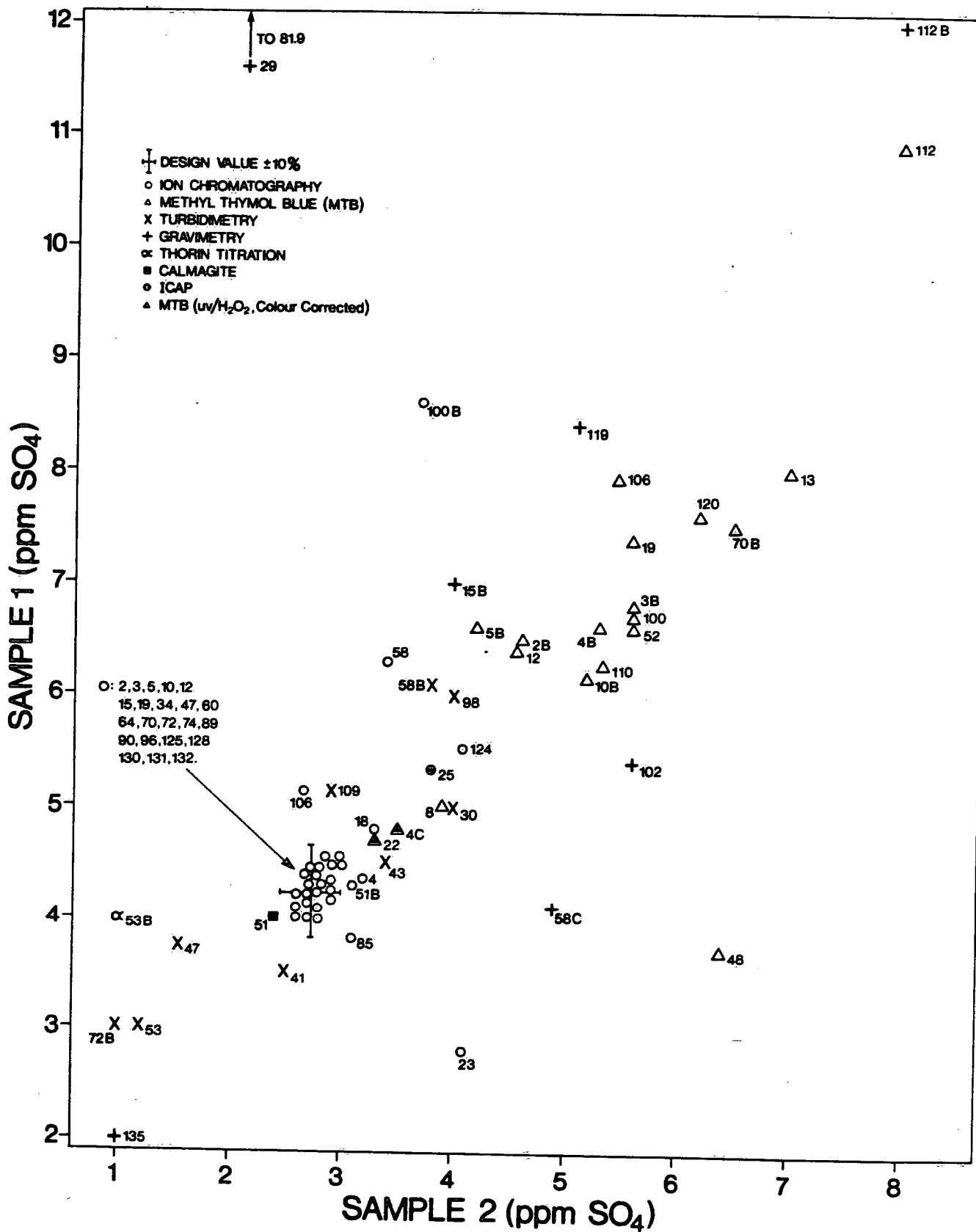


FIGURE 1. PAIRED SAMPLE PLOT FOR SAMPLES 2 AND 1

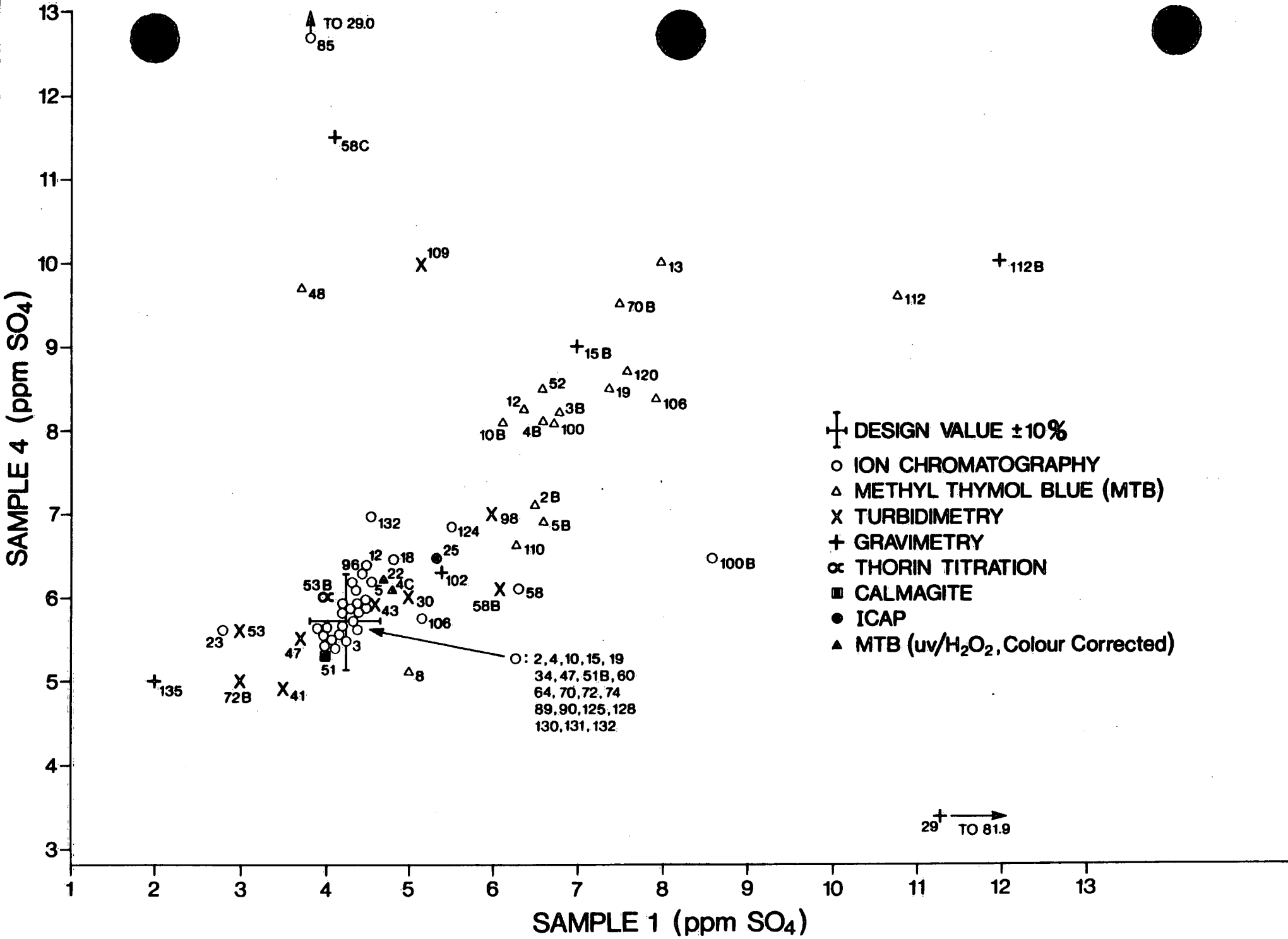


FIGURE 2. PAIRED SAMPLE PLOT FOR SAMPLES 1 AND 4

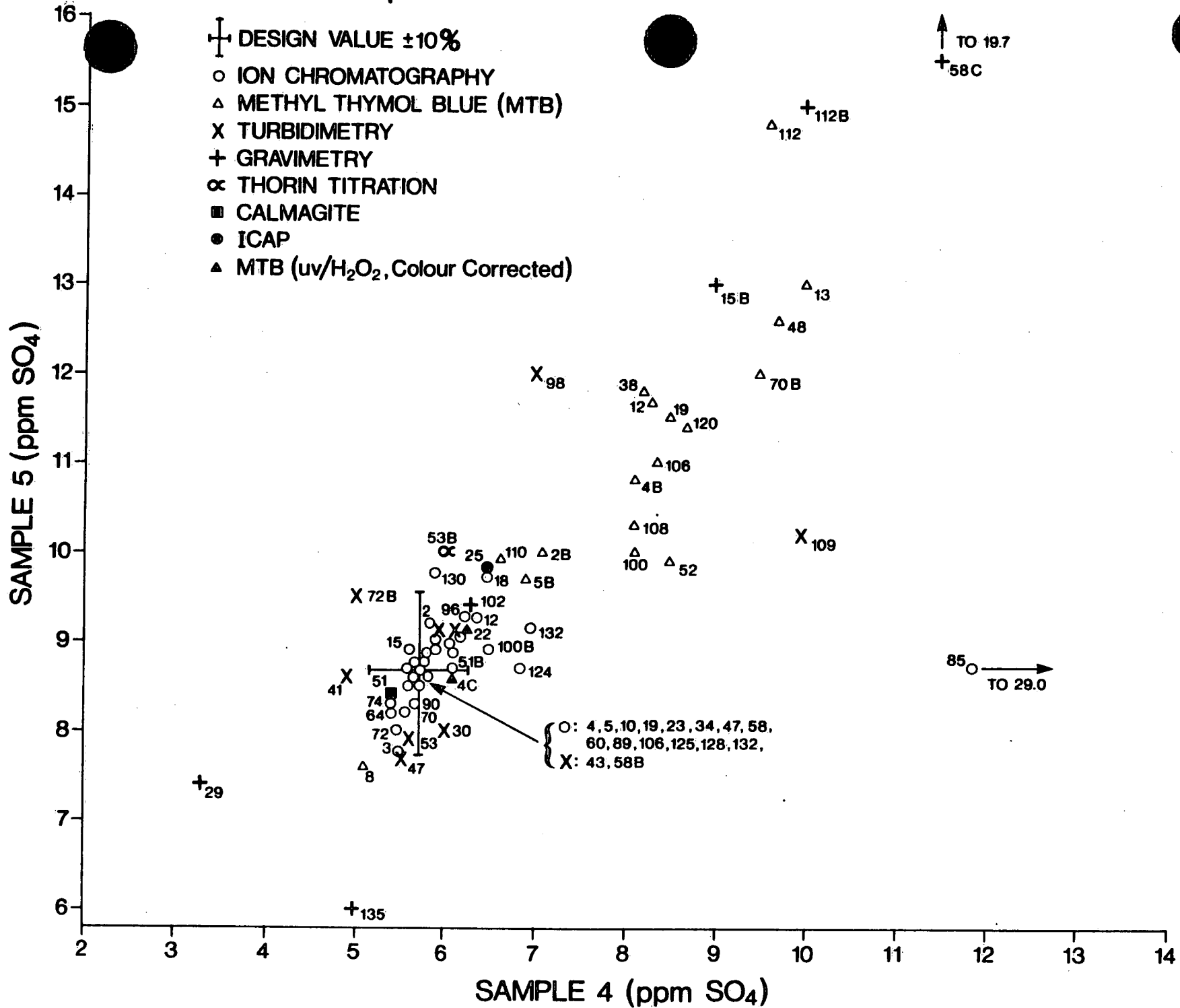


FIGURE 3. PAIRED SAMPLE PLOT FOR SAMPLES 4 AND 5

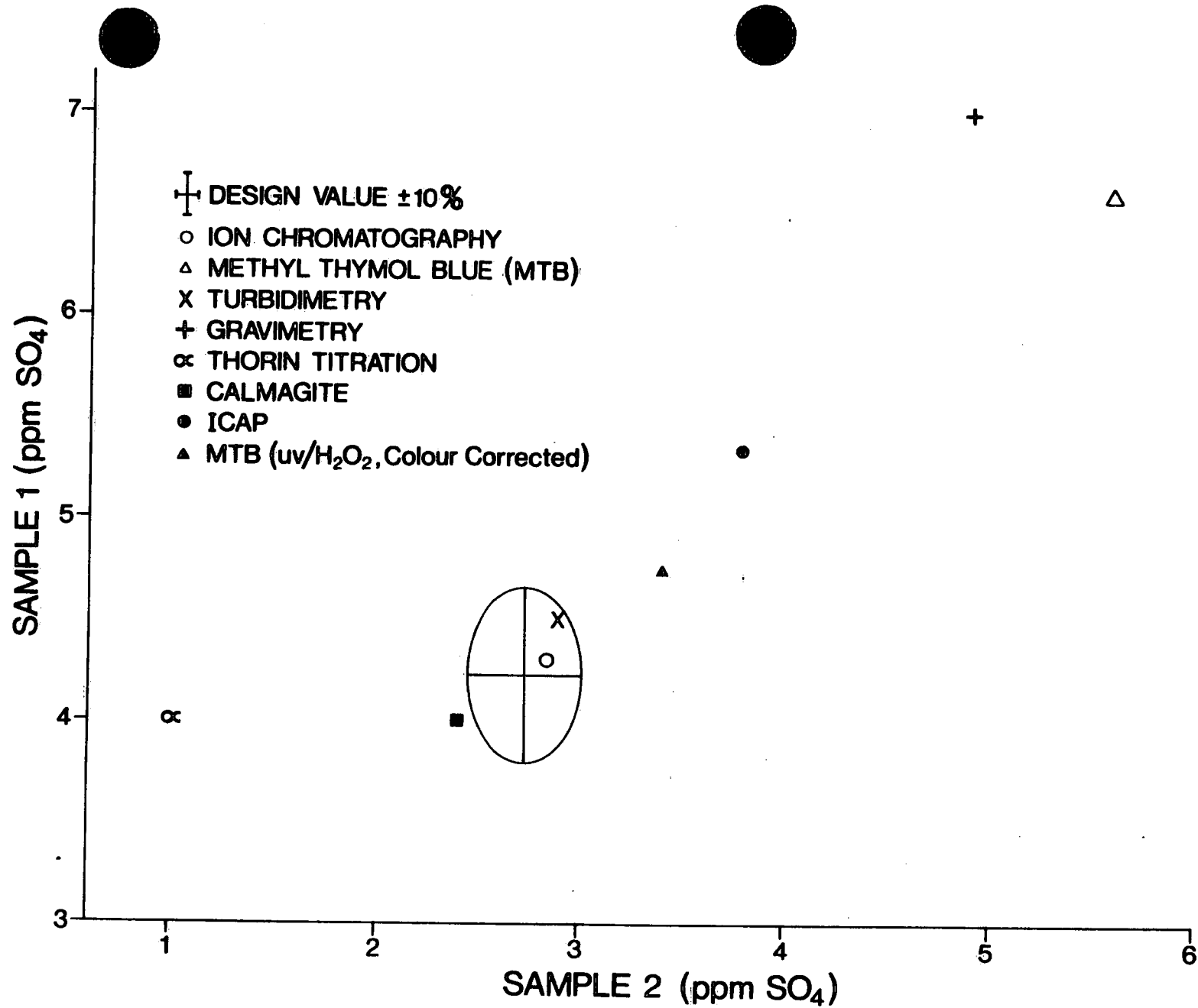


FIGURE 4. COMPARISON OF THE DESIGN VALUE WITH MEDIAN VALUES IN PAIRED SAMPLES 2 AND 1 DETERMINED BY VARIOUS METHODOLOGIES

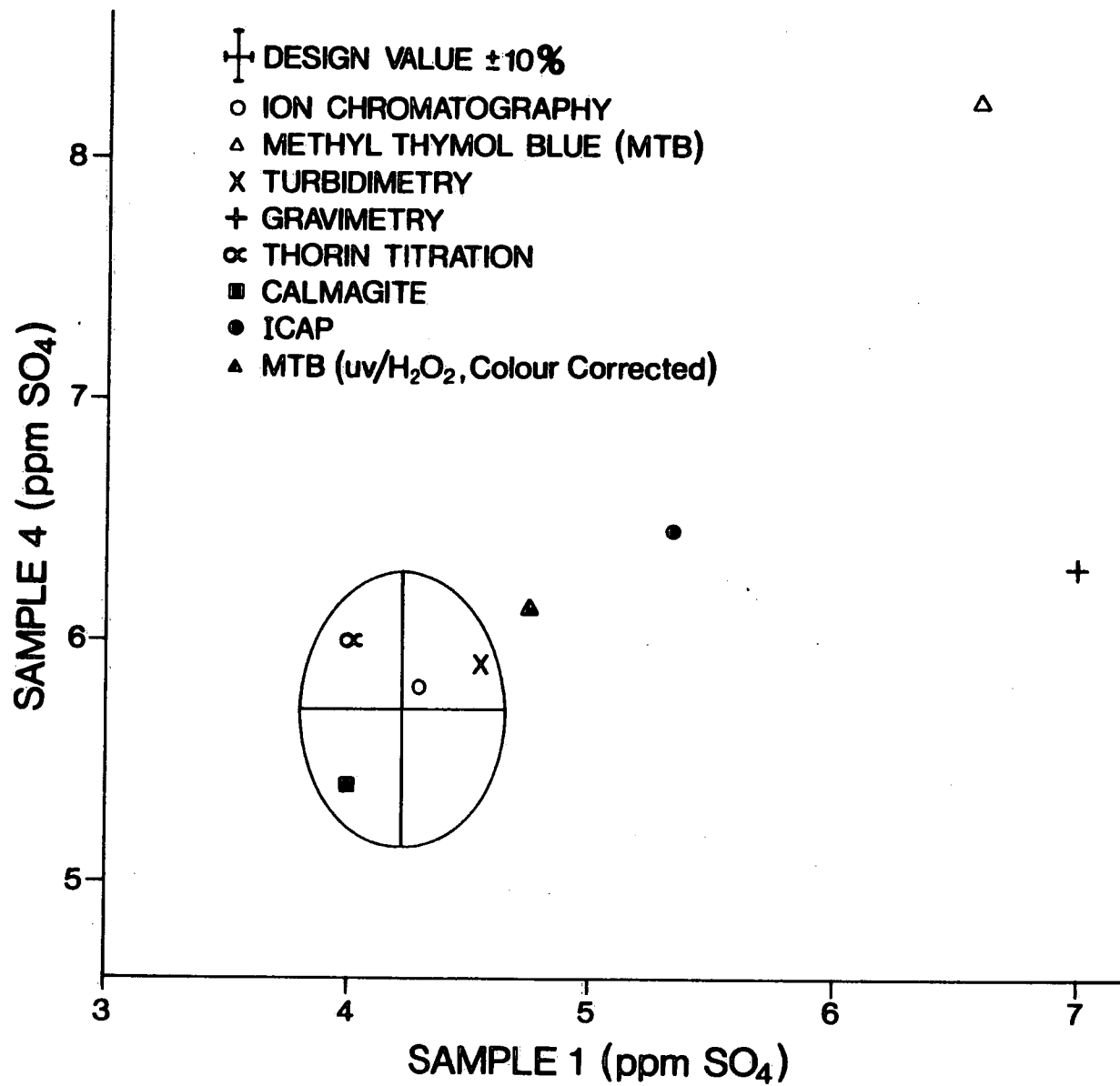


FIGURE 5. COMPARISON OF THE DESIGN VALUE WITH MEDIAN VALUES IN PAIRED SAMPLES 1 AND 4 DETERMINED BY VARIOUS METHODOLOGIES

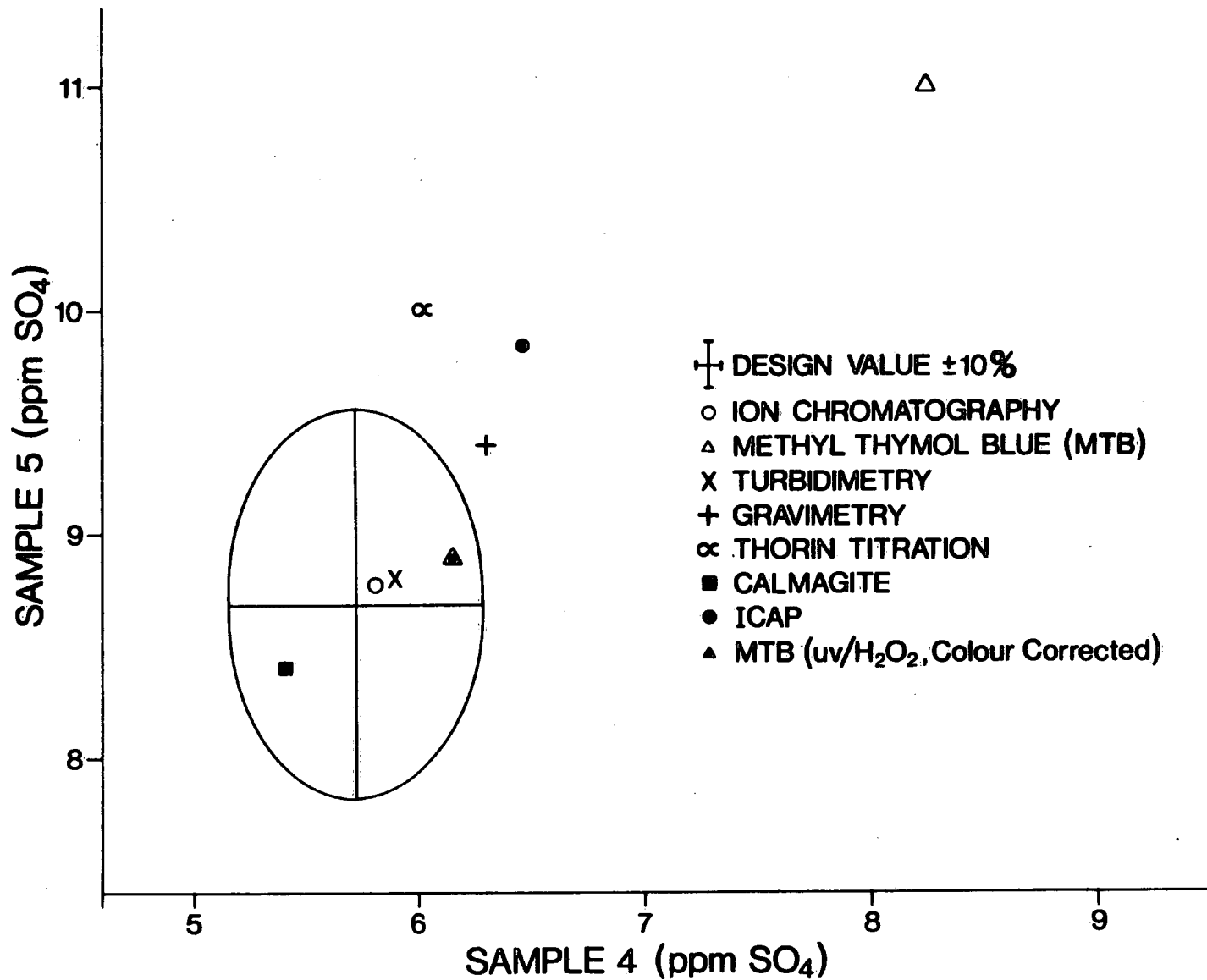


FIGURE 6 . COMPARISON OF THE DESIGN VALUE WITH MEDIAN VALUES IN PAIRED SAMPLES 4 AND 5 DETERMINED BY VARIOUS METHODOLOGIES

