COMPARISON OF X-RAY FLUORESCENCE TECHNIQUES BY FUSED GLASS DISCS AND INDUCTIVELY COUPLED PLASMA (ICP) FOR CHEMICAL ANALYSIS OF DRILL HOLE SAMPLES [1]

Mário Alzamora Gomes [2]

Abstract

The possible existence of bias and precision differences between the techniques of X-ray Fluorescence by fused glass discs and Plasma (ICP) for the chemical analysis of SiO_2, P, Al_2O_3, Mn, CaO, MgO and TiO_2 in drill hole samples has been investigated. Identical pulverized samples were analyzed in an interlaboratory program by laboratories that use X-ray and Plasma. The data generated were analyzed in graphs 1:1, Student Test-t and by applying ISO standards for precision and bias calculation. There is no meaningful trend toward any of the elements when data behavior is observed for the entire analytical range. However, for some elements, statistically meaningful differences have been observed for the average and/or precision. These differences were appraised using as a reference the pertinent ISO standards and also by the team responsible for the geological database for the acceptance of analytical results.

Key words: Drill hole; Plasma; X-ray

Resumo

A possível existência de vício e diferenças de precisão entre as técnicas de Fluorescência de Raios-X por pastilha fundida e Plasma (ICP) para análise química de SiO_2, P, Al_2O_3, Mn, CaO, MgO e TiO_2 em amostras de furos de sondagem foi investigada. Amostras pulverizadas idênticas foram analisadas num programa interlaboratorial por laboratórios que utilizam RX e Plasma. Os dados gerados foram analisados em gráficos 1:1, Teste-t de Student e pela aplicação de normas ISO para cálculo da precisão e vício. Não existe tendência significativa para nenhum dos elementos quando se observa o comportamento dos dados para a faixa analítica inteira. Entretanto, para alguns elementos diferenças estatisticamente significativas foram observadas, para a média e/ou precisão Essas diferenças foram avaliadas tendo-se como referência as normas ISO pertinentes e também pela equipe responsável pelo banco de dados geológico para a aceitação dos resultados analíticos.

Palavras-chave: Furos de sondagem; Plasma; Raios-X.

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2 *Chemical Engineer, Companhia Vale do Rio Doce, Itabira/MG, Brazil.*

1 INTRODUCTION

Vale's laboratories in Minas Gerais render chemical and granulometric analyses services of drill hole samples from mines located in the State.

For SiO_2, P, Al_2O_3, Mn, CaO, MgO and TiO_2 two analytical techniques are employed by the laboratories according to equipment availability: X-ray Fluorescence Spectrometry with fused glass discs (Fusion) and Optical Emission Spectrometry with Inductively Coupled Plasma (Plasma).

In order to enjoy greater operating flexibility, Vale is interested in applying the two techniques, indistinctly, which would make feasible, for example, the transfer of samples from one laboratory to the other, considering lab demand and capacity. To accomplish that, it is necessary to demonstrate that Fusion and Plasma show coherent results between them, without bias and with compatible precision, to preclude an impact to the Geology database for the Drill hole samples.

In order to attain this objective an interlaboratory program was carried out where 756 samples were selected in varying granulometric ranges, the mines of origin and element contents to cover the whole analytical universe.

2 MATERIALS AND METHODS

To conduct the experiment Vale's laboratories prepared, for each sample, two identical aliquots of pulverized ore at -45 μm, which were distributed to two company laboratories, and each one performed the analyses in duplicate using its routine technique, Fusion or Plasma. The data were treated statistically using the 1:1 graphs, paired t-test, and bias test following ISO 3086:2006. The results were also compared with ISO standards for Fusion and Plasma analyses. Finally, the results were submitted to a team of geologists to be validated conforming to the client's view.

3 RESULTS AND DISCUSSION

The analytical ranges of each one of the chemical elements evaluated are too large. In order to have a more detailed interpretation, the analytical ranges have been divided into four smaller ranges and a complete study was carried out for each of these ranges. This procedure has the advantage of enabling the comparison of Fusion and Plasma techniques in a more specific way, that is, with regards to their analytical contents. The first six columns in Table 1 display, for Fusion and Plasma, the analytical ranges considered, the number of samples and the average content for each. In view of the large number of samples it was not possible to include all data in this work, only the averages have been informed. On the line of Totals, the Interval represents lower and higher values of each element.

The graphs and statistical tests have been carried out with the aid of Minitab software, version 14. The level of significance adopted was 5%.

Table 1. Plasma x Fusion Comparative Results

SiO_2	Analytical range	Interval (%)	Number of samples	Analytical technique	Average content (%)	Paired t-test	Absolute bias (%)	δ minimum	Reproducibility ISO Standards	Variance	β_M	β_M ISO Standards
	1	0 - 2,00	195	Fusion	0,99	Equal	0,01	0,02	0,05	3,20E-04	0,04	0,03
				Plasma	0,98				0,15	7,00E-05	0,02	0,05
	2	2,01 - 6,00	346	Fusion	3,65	Equal	0,01	0,02	0,09	6,10E-04	0,05	0,06
				Plasma	3,66				0,15	3,20E-04	0,04	0,08
	3	6,01 - 20,00	144	Fusion	11,32	Equal	0,04	0,08	0,18	2,50E-03	0,10	0,14
				Plasma	11,36				0,15	1,61E-03	0,08	0,13
	4	>20,00	71	Fusion	35,93	**Different**	0,20	0,33	0,49	1,21E-02	0,22	0,41
				Plasma	36,13				0,15	4,71E-03	0,14	0,22
	Total	0,18 - 71,76	756	Fusion	7,46	-	0,02	-	-	1,28E-03	0,07	-
				Plasma	7,48					5,93E-04	0,05	

P	Analytical range	Interval (%)	Number of samples	Analytical technique	Average content (%)	Paired t-test	Absolute bias (%)	δ minimum	Reproducibility ISO Standards	Variance	β_M	β_M ISO Standards
	1	0 - 0,020	181	Fusion	0,015	Equal	0,001	0,001	0,002	2,71E-07	0,001	0,001
				Plasma	0,014				0,176	7,85E-07	0,002	0,001
	2	0,021 - 0,040	259	Fusion	0,031	Equal	0,000	0,001	0,002	2,57E-07	0,001	0,001
				Plasma	0,031				0,177	7,26E-07	0,002	0,002
	3	0,041 - 0,060	176	Fusion	0,050	Equal	0,001	0,002	0,002	3,39E-07	0,001	0,001
				Plasma	0,049				0,177	8,87E-07	0,002	0,003
	4	>0,060	140	Fusion	0,078	Equal	0,000	0,002	0,003	6,72E-07	0,002	0,002
				Plasma	0,078				0,178	1,77E-06	0,003	0,004
	Total	0,005 - 0,147	756	Fusion	0,040	-	0,000	-	-	3,43E-07	0,001	-
				Plasma	0,040					9,40E-07	0,002	

Al_2O_3	Analytical range	Interval (%)	Number of samples	Analytical technique	Average content (%)	Paired t-test	Absolute bias (%)	δ minimum	Reproducibility ISO Standards	Variance	β_M	β_M ISO Standards
	1	0 - 0,50	271	Fusion	0,33	**Different**	0,00	0,02	0,02	3,20E-05	0,01	0,02
				Plasma	0,33				0,03	1,68E-05	0,01	0,01
	2	0,51 - 1,50	342	Fusion	0,88	**Different**	0,01	0,02	0,03	8,37E-05	0,02	0,03
				Plasma	0,89				0,06	6,12E-05	0,02	0,02
	3	1,51 - 3,00	112	Fusion	1,95	Equal	0,00	0,03	0,05	2,01E-04	0,03	0,04
				Plasma	1,95				0,12	1,48E-04	0,02	0,04
	4	>3,00	31	Fusion	6,06	Equal	0,04	0,11	0,12	1,22E-03	0,07	0,09
				Plasma	6,10				0,36	1,08E-03	0,07	0,10
	Total	0,12 - 9,81	756	Fusion	1,06	-	0,00	-	-	9,41E-05	0,02	-
				Plasma	1,06					6,66E-05	0,02	

Mn	Analytical range	Interval (%)	Number of samples	Analytical technique	Average content (%)	Paired t-test	Absolute bias (%)	δ minimum	Reproducibility ISO Standards	Variance	β_M	β_M ISO Standards
	1	0 - 0,100	291	Fusion	0,037	**Different**	0,001	0,002	0,002	6,32E-07	0,002	0,002
				Plasma	0,036				0,006	3,94E-07	0,001	0,002
	2	0,101 - 0,500	391	Fusion	0,239	**Different**	0,003	0,004	0,008	5,36E-06	0,005	0,007
				Plasma	0,236				0,018	4,55E-06	0,004	0,010
	3	0,501 - 2,000	45	Fusion	0,786	**Different**	0,017	0,031	0,025	1,83E-05	0,009	0,022
				Plasma	0,769				0,050	2,18E-05	0,009	0,030
	4	> 2,000	29	Fusion	8,18	**Different**	0,180	0,285	0,250	6,94E-04	0,053	0,223
				Plasma	8,00				0,486	8,91E-04	0,060	0,309
	Total	0,002 - 13,55	756	Fusion	0,498	-	0,009	-	-	7,66E-06	0,006	-
				Plasma	0,489					7,66E-06	0,006	

CaO	Analytical range	Interval (%)	Number of samples	Analytical technique	Average content (%)	Paired t-test	Absolute bias (%)	δ minimum	Reproducibility ISO Standards	Variance	β_M	β_M ISO Standards
	1	0 - 0,010	171	Fusion	0,009	**Different**	0,002	0,003	0,005	6,23E-07	0,002	0,003
				Plasma	0,007				0,006	6,29E-07	0,002	0,002
	2	0,011 - 0,020	294	Fusion	0,015	Equal	0,001	0,002	0,005	8,90E-07	0,002	0,003
				Plasma	0,014				0,012	1,43E-06	0,002	0,005
	3	0,021 - 0,030	112	Fusion	0,025	Equal	0,000	0,002	0,005	1,37E-06	0,002	0,004
				Plasma	0,025				0,016	2,19E-06	0,003	0,007
	4	> 0,030	179	Fusion	0,291	**Different**	0,005	0,010	0,008	6,43E-06	0,005	0,005
				Plasma	0,296				0,036	1,31E-05	0,007	0,017
	Total	0,003 - 2,94	756	Fusion	0,080	-	0,001	-	-	1,74E-06	0,003	-
				Plasma	0,081					2,96E-06	0,003	

Table 1 (cont'd). Plasma x Fusion Comparative Results

	Analytical range	Interval (%)	Number of samples	Analytical technique	Average content (%)	Paired t-test	Absolute bias (%)	δ minimum	Reproducibility ISO Standards	Variance	β_M	β_M ISO Standards
MgO	1	0 - 0,020	177	Fusion	0,011	Equal	0,001	0,003	0,032	2,26E-06	0,003	0,018
				Plasma	0,012				0,002	2,87E-07	0,001	0,001
	2	0,021 - 0,040	296	Fusion	0,031	Equal	0,002	0,003	0,033	5,14E-06	0,005	0,002
				Plasma	0,029				0,005	5,51E-07	0,001	0,001
	3	0,041 - 0,060	121	Fusion	0,050	**Different**	0,005	0,007	0,033	5,12E-06	0,005	0,018
				Plasma	0,045				0,007	9,49E-07	0,002	0,002
	4	> 0,060	162	Fusion	0,186	Equal	0,004	0,008	0,037	1,46E-05	0,008	0,020
				Plasma	0,182				0,022	2,40E-06	0,003	0,008
	Total	0,002 - 1,030	756	Fusion	0,062	-	0,002	-	-	5,85E-06	0,005	-
				Plasma	0,060					8,17E-07	0,002	

	Analytical range	Interval (%)	Number of samples	Analytical technique	Average content (%)	Paired t-test	Absolute bias (%)	δ minimum	Reproducibility ISO Standards	Variance	β_M	β_M ISO Standards
TiO_2	1	0 - 0,050	389	Fusion	0,037	**Different**	0,003	0,004	0,006	7,37E-06	0,005	0,003
				Plasma	0,034				0,016	2,25E-07	0,001	0,003
	2	0,051 - 0,100	274	Fusion	0,070	**Different**	0,003	0,005	0,006	7,79E-06	0,006	0,004
				Plasma	0,067				0,016	6,38E-07	0,002	0,004
	3	0,101 - 0,250	77	Fusion	0,137	Equal	0,005	0,009	0,008	1,13E-05	0,007	0,004
				Plasma	0,132				0,016	3,31E-06	0,004	0,005
	4	> 0,250	16	Fusion	0,859	**Different**	0,036	0,055	0,025	9,40E-05	0,019	0,010
				Plasma	0,823				0,016	5,11E-05	0,014	0,011
	Total	0,002 - 1,368	756	Fusion	0,076	-	0,004	-	-	8,74E-06	0,006	-
				Plasma	0,072					7,57E-07	0,002	

3.1. Graphs 1:1

In graphs 1:1 Fusion and Plasma results are plotted respectively on the ordinate and abscissa axes, in increasing order of values. One line 1:1 with a slant of 45 degrees is projected as a reference, and represents the ideal situation: Fusion and Plasma identical results. The graphs are displayed in Figure 1.

It can be noted that in none of the elements analyzed there are indications of bias when considering the entire analytical range, although there are some points that could be considered outliers. These outliers are, nonetheless, rare events and may be credited to punctual analytical errors which do not interfere in the general conclusion of absence of bias between the two analytical techniques.

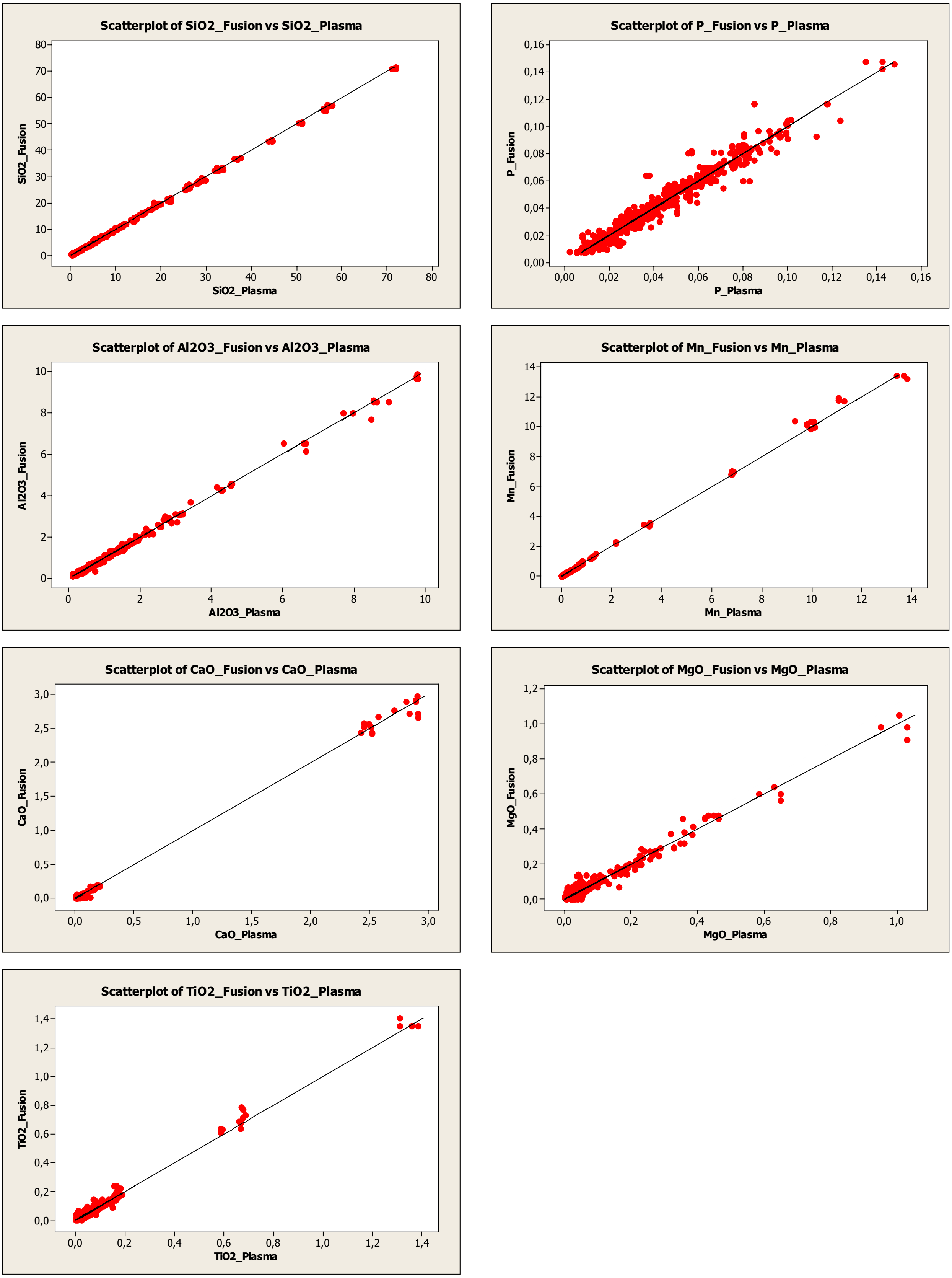

Figure 1. Graphs 1:1 – Fusion x Plasma.

3.2 Paired t-Test

The paired Student t-Test, at the 5% level of significance was employed to appraise statistical differences between Fusion and Plasma for the elements analyzed in each of the analytical ranges. Since the analyses were performed in duplicate, we used the averages of each sample to form the Fusion x Plasma pairs. The results are displayed in Table 1 (the first of the green columns).

With the exception of P all other elements displayed at least one of the ranges with rejection to the t-Test, that is, there is significant statistical difference between Fusion and Plasma techniques in many situations. It is necessary then a complement of the investigative process: to evaluate whether the meaningful differences are also statistically meaningful under the chemical analysis point of view.

It is worth pointing out here that all test results are released only when the results of one or more certified reference materials that accompany sample analysis are found within previously defined tolerance limits.

Deviations may be the result of gauging details, constructive aspects of weighing and measuring equipment, of the analytical method itself, of the analyst who performs the tests, the quality of the lot of reagents or simply due to random variables that escape lab control and which act in predetermined periods.

For comparison purposes, absolute bias (second green column in Table 1) were confronted with reproducibility values between laboratories indicated in pertinent ISO standards: ISO 9516-1: 2003 (X-ray Spectrometry with fused glass discs) and ISO/DIS 11535: 2006 (Plasma) and also with acceptable bias values calculated following ISO 3086:2006, according to items 3.3 and 3.4.

3.3 Comparison of Bias with ISO Standards

There are no acceptable limits in ISO standards for different results between two analytical techniques. In this work we chose to consider Reproducibility values (P) between laboratories, calculated from equations of ISO standards 9516-1: 2003 (Fusion) and ISO/DIS 11535: 2006 (Plasma) as being acceptable limits for the difference between Plasma and Fusion (last green column in Table 1).

Only in two situations the absolute slant stands over ISO standard reproducibility limits:

a) SiO_2 >20%: the absolute bias of 0.20% is over the reproducibility indicated for Plasma, which is 0.15%;
b) TiO_2 >0,250%: the absolute bias of 0.036% is over the reproducibility indicated for Fusion and Plasma, respectively 0.025% and 0.016%.

In house studies are being carried out aiming at minimizing these differences, such as the implementation of X-ray curves for calcined fused glass discs and recalibration with inclusion of new points for X-ray curves and Plasma. Without regard to the conclusion of these works it is necessary the discussion of these differences with the information client, in this case the Geology team. The geologists considered acceptable the bias noted.

3.4 Bias Test Acceptable According to ISO 3086

The purpose of ISO 3086:2006 is to appraise the bias of a sampling system in comparison with a reference sampling. However, it has been routinely used to evaluate distortions of any magnitude since it inserts the concept of acceptable absolute bias (δ) from which two sets of data may be considered equivalent. This procedure is more attuned with lab reality, since we know that small distortions are frequently tolerable by the information client.

Hence, for each one of the analytical ranges, the value of δ minimum was established and included in Table 1 (third green column). These values were submitted to the team responsible for the geological database for a careful forethought. The geologists' opinion is that the biases displayed are acceptable; they do not jeopardize the quality of database nor impair the evaluation job of reserves. For comparison purposes the values of Absolute Bias obtained in the interlaboratory program were indicated in Table 1 in the column prior to that of δ minimum values.

3.5 Evaluation of Precision (β_M)

From the results of duplicates, the β_M Measurement Precision for each analytical range was estimated for Fusion and Plasma techniques. The Measurement Precision represents the 95% confidence interval for the analysis results and was calculated from the variance values (first gray column in Table 1), following ISO 3085:2002. The values come upon were recorded in the second gray column in Table 1 and are graphically shown in Figure 2.

It is noted that the techniques alternate among the best precisions. Plasma has better precision for SiO_2, MgO e TiO_2, whereas Fusion has better precision for P and CaO. For Mn and Al_2O_3 precisions are similar for the two techniques.

Once again the team responsible for the geologic database was called upon to appraise the calculated measurement precision values. The conclusion arrived at was that the values are relatively small in comparison with average contents. Therefore, despite existing precision differences, the two techniques are acceptable for the performance of chemical analyses of drill hole samples and do not jeopardize database integrity and reliability.

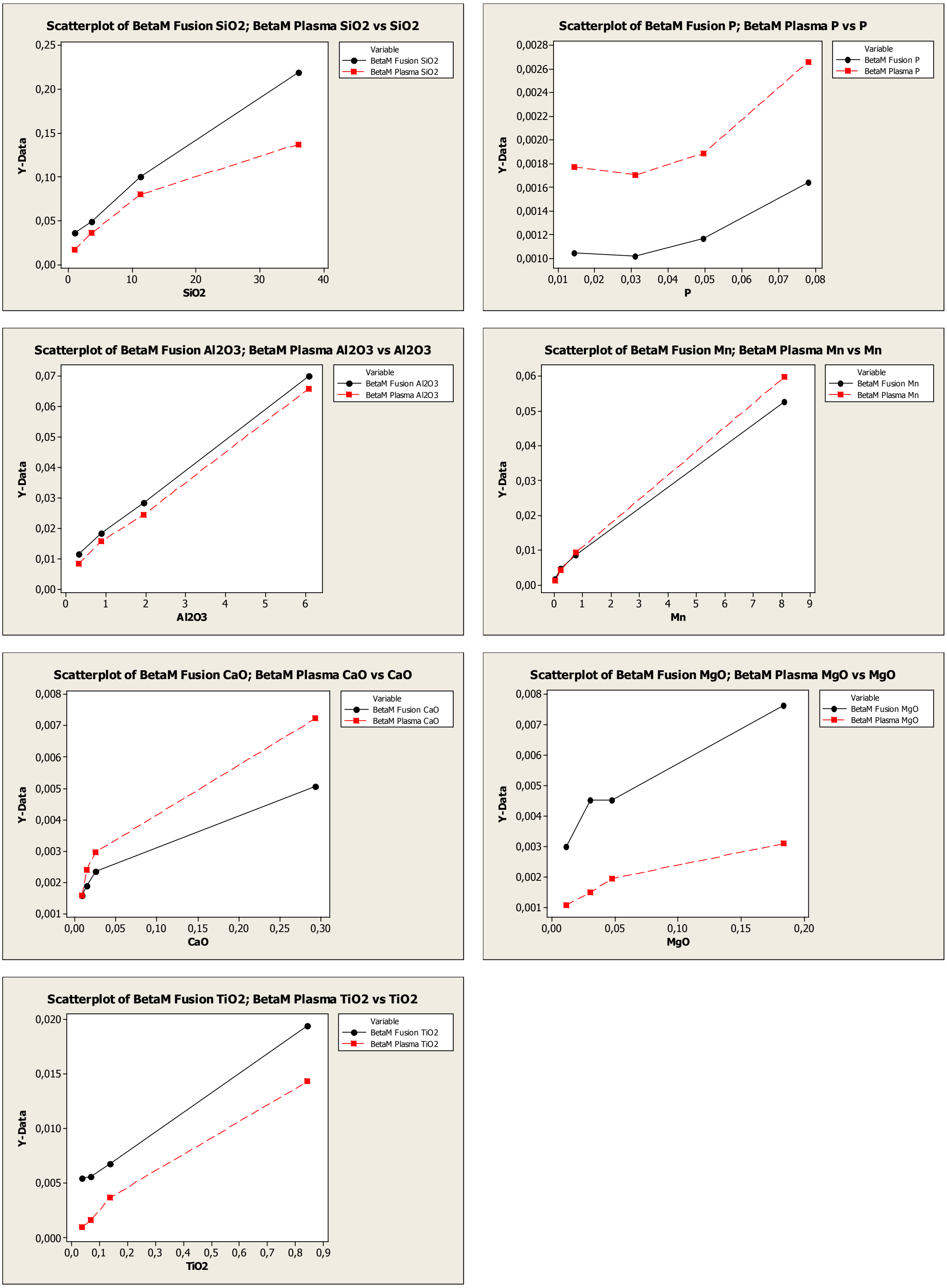

Figure 2. β_M graphs in relation to element contents (Plasma x Fusion)

3.6 β_M Precision Comparison with ISO Standards

β_M precisions obtained from the interlaboratory program were compared with the precisions indicated in ISO standards 9516-1: 2003 (Fusion) and ISO/DIS 11535: 2006 (Plasma), the latter recorded in the last gray column in Table 1. For SiO_2, P and MgO only one occurrence of precision over the standard was noted, considering the little relevance to influence the geologic database. Nevertheless, internal works were initiated to evaluate the matter in depth, which includes changes in sample/flux relationship, adjustments in the disk making machine, among others. The problem that attracted more attention was the TiO_2 case where various precision situations cropped up worse than those expected by ISO standards, especially for Fusion. Preliminary works showed strong influence of the tense active agent (potassium iodide) used to facilitate the removal of the glass disk from the mould, on the TiO_2 results. Substitution of the tense active agent or change in its concentration is being evaluated. As previously commented, these results do not produce a meaningful impact on the geologic database, per the evaluation of the team of geologists.

4 CONCLUSIONS

Fusion and Plasma techniques show some differences in terms of average results and precision for some of the elements normally analyzed in drill hole samples. These differences were statistically analyzed, compared with acceptable values anticipated in ISO standards and finally submitted to the final assessment of the team of geologists responsible for the geologic database.

The conclusion arrived at is that despite some meaningful statistically differences found it is possible to accept the analytical equivalence between the two techniques, since they do not impact negatively on reserve assessments based on the geologic database.

REFERENCES

1 ISO 3085:2002: Iron ores -- Experimental methods for checking the precision of sampling, sample preparation and measurement;
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3 ISO/DIS 11535: 2006: Iron ores -- Determination of various elements – Inductively coupled plasma atomic emission spectrometric method;
4 ISO 9516-1: 2003: Iron ores -- Determination of various elements by X-ray fluorescence spectrometry – Part 1: Comprehensive procedure.