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**Interference from Calcium, Iron and Magnesium
on Lead, Zinc, and Silver AAS Analyses**

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INTERFERENCE FROM CALCIUM, IRON, AND MAGNESIUM ON LEAD, ZINC, AND SILVER AAS ANALYSES

I N T R O D U C T I O N

In 1965 Billings (p 357-361) reported what is probably the "... first true matrix absorption" in AAS analyses (Capacho-Delgado and Sprague, 1965, p 364). Billings reported that Ca, Mg, Na, K, and Fe interfere with the analyses of Bi, Cu, Mn, Zn, Ba, Fe, Ca, Cd, Ni, and Pb. He found that Ca and Mg were the strongest interferents, followed by Fe. Billings' interpretation was that the interfering elements gave rise to absorption bands from such species as CaOH which were not fully vaporized in the flame. This causes light scattering which is registered on the AA read-out as absorption. Capacho-Delgado and Sprague (1965, p 364) confirmed Billings' results and suggested that a much higher temperature flame, such as that from nitrous oxide, might eliminate the problem by vaporizing the interfering species.

The interference problem is significant only in trace or very high accuracy analyses. Geochemical analyses are trace element analyses and the magnitude of the interference that is suggested is significant. We have noticed the interference while running geochemical analyses for Pb, Zn, and Ag on carbonate and ferruginous samples. This report covers our investigation of the magnitude of the interference from Ca, Mg, and Fe on Pb, Zn, and Ag, and a suggestion of a method of control. We have also found a strong interference of Fe on Au, which is not investigated in this study. This interference prevents the accurate analysis for gold on Fe-containing sample solutions. Iron interference is controlled in our gold analyses by extracting the gold into the organic reagent methyl isobutyl ketone and then removing iron from the organic with a 0.1 N HCL wash.

E X P E R I M E N T A L

Matthey "Spec Pure" reagents were used to form master solutions of Ca, Mg, and Fe. The concentrations were designed to represent the maximum of each of these elements that would be present in solutions from calcite (Ca), dolomite (Mg), or hematite (Fe). A series of dilutions of the master solutions formed solutions of diminishing content of each interfering element. All these solutions should be essentially free from Pb, Zn, or Ag because of the high purity of the reagents used, and so any registered absorbance on the analytical lines would represent interference.

Each solution was asperated on the analytical lines of Pb, Zn, and Ag to determine the magnitude of the interference. Table 1 shows the compositions of the solutions, the absorbance read, and apparent ppm concentration caused by the interfering element. The apparent concentrations shown in table 1 are the concentrations that would be indicated to be in the sample (10 gram sample in 100 ml of liquor) when actually there were none of the elements present. That is, concentrations indicated solely because of the positive interference of the matrix elements. Table 1 shows that the magnitude of the interference is significant for geochemical analyses. A pure hematite sample would indicate 27.5 ppm Zn, 9.0 ppm Pb, and 1.4 ppm Ag with none of those elements present. A pure calcite sample would indicate 2.9 ppm Zn, 15 ppm Pb, and 1.7 ppm Ag with none of those elements present. A dolomite sample would indicate 8.2 ppm Pb and 1.7 ppm Ag from the Mg content of dolomite. The Mg solutions were accidentally destroyed before the Zn interference could be determined, but we guess it would be about half the magnitude of calcium, or about 1.5 ppm indicated Zn at maximum Mg from dolomite.

C O N T R O L O F T H E I N T E R F E R E N C E S

Billings (1965, p 360) found that for some of the elements a nearby non-absorbing line for the element could be used to control the interference. By measuring the absorbance on a nonabsorbing line the level of interference is indicated. This is true because on a nonabsorbing line there should be zero absorbance. Capacho-Delgado and Sprague pointed out that the non-absorbing line must be near the absorbing line because the strength of the interference absorption band varies across the spectrum (p 363, fig 1). For Ag and Zn no nearby nonabsorbing lines exist.

We have devised a method which, though not precise, is an approximation for the needed correction. To correct for the presence of Fe we make a visual estimate of the iron concentration by comparing the color of the solution to solutions of known iron concentration. From the data of table 1 a plot of the correction needed vs iron concentration can be formed (fig 2). The presence of high Ca in the analyte is readily detected because the flame assumes a red color. For Ca correction we determine the absorbance on the Zn 3074Å nonabsorbing line, and from that absorbance make an estimate of the calcium level from a graph of absorbance on 3074Å Zn vs calcium concentration (fig 1).

For example, if significant iron is present but no significant calcium, we estimate the iron concentration by liquor color and then apply the correction indicated in figure 2 for each of the elements. If significant calcium is present we determine the absorption on the Zn 3074Å line and use figure 1 to estimate the Ca concentration. Knowing the Ca concentration, figure 2 is then used to arrive at a correction. An added complication, uncommon but entirely possible, is when both Fe and Ca are present at significant levels. In such a case the iron can be estimated visually, the iron curve of figure 1 used to subtract the absorbance due to iron and the remaining absorbance attributed to Ca to determine the Ca level. Any Mg interference in this scheme is read as Ca and introduces some error.

The only samples that need the above treatment are those that are rather high in Fe and/or Ca. Generally, the high calcium samples will not also be high in Fe, and so only one of the corrections need be applied. Table 2 shows some minimum chemical and mineralogic compositions that would lead to "significant" interference and represent compositions above which we would be inclined to apply the correction procedure for geochemical samples. For lead, for example, we would apply a correction above 26% hematite and 16% calcite. Table 2 shows other minimums beyond which we would apply the correction for geochem samples.

Our suggested method for correcting the interference is neither elegant nor precise but it does help and may be precise enough for geochemical applications. We are looking for a better method short of having to analyze separately to determine the concentrations of the interfering elements.

Table 1
ABSORBENCE AND APPARENT CONCENTRATION DATA

INTERFERENT AND CONCENTRATION PPM	ABSORBENCE AND APPARENT PPM IN SAMPLE					
	Zn LINE 2139Å	APPARENT* PPM Zn	Pb LINE 2833Å	APPARENT* PPM Pb	Ag LINE 3281Å	APPARENT* PPM Ag
Ca 40,000	0.055	2.9	0.045	15.0	0.055	1.7
20,000	0.050	2.6	0.025	8.0	0.020	0.7
10,000	0.040	2.0	0.010	3.0	0.010	0.3
5,000	0.025	1.3	0.008	2.5	0.007	0.2
2,500	0.020	1.0	0.005	1.5	0.005	0.1
625	-----	---	0.003	0.7	0.000	0.0
312	0.005	0.2	0.000	0.0		
Mg 15,000			0.025	8.2	0.010	0.3
7,500	Sample		0.015	5.0	0.000	0.0
3,750	Solution		0.010	3.0		
1,875	Lost		0.002	0.7		
937			0.000	0.0		
468			-----	---		
Fe 70,000	0.47	27.5	0.027	9.0	0.045	1.4
35,000	0.32	18.9	0.015	5.0	0.030	1.0
17,500	0.195	11.2	0.010	3.1	0.015	0.5
8,750	0.140	8.0	0.005	1.5	0.005	0.2
4,375	0.100	5.8	-----	---	0.000	0.0
2,187	0.065	3.4	-----	---		
1,093	-----	-----	0.002	0.7		
546	0.050	1.6	0.000	0.0		
273	0.030	1.0				

* The "apparent" concentration is the metal level indicated to be in the sample considering a 10 gram sample taken to 100 ml of solution.

- Calcium
- △ Magnesium
- Iron

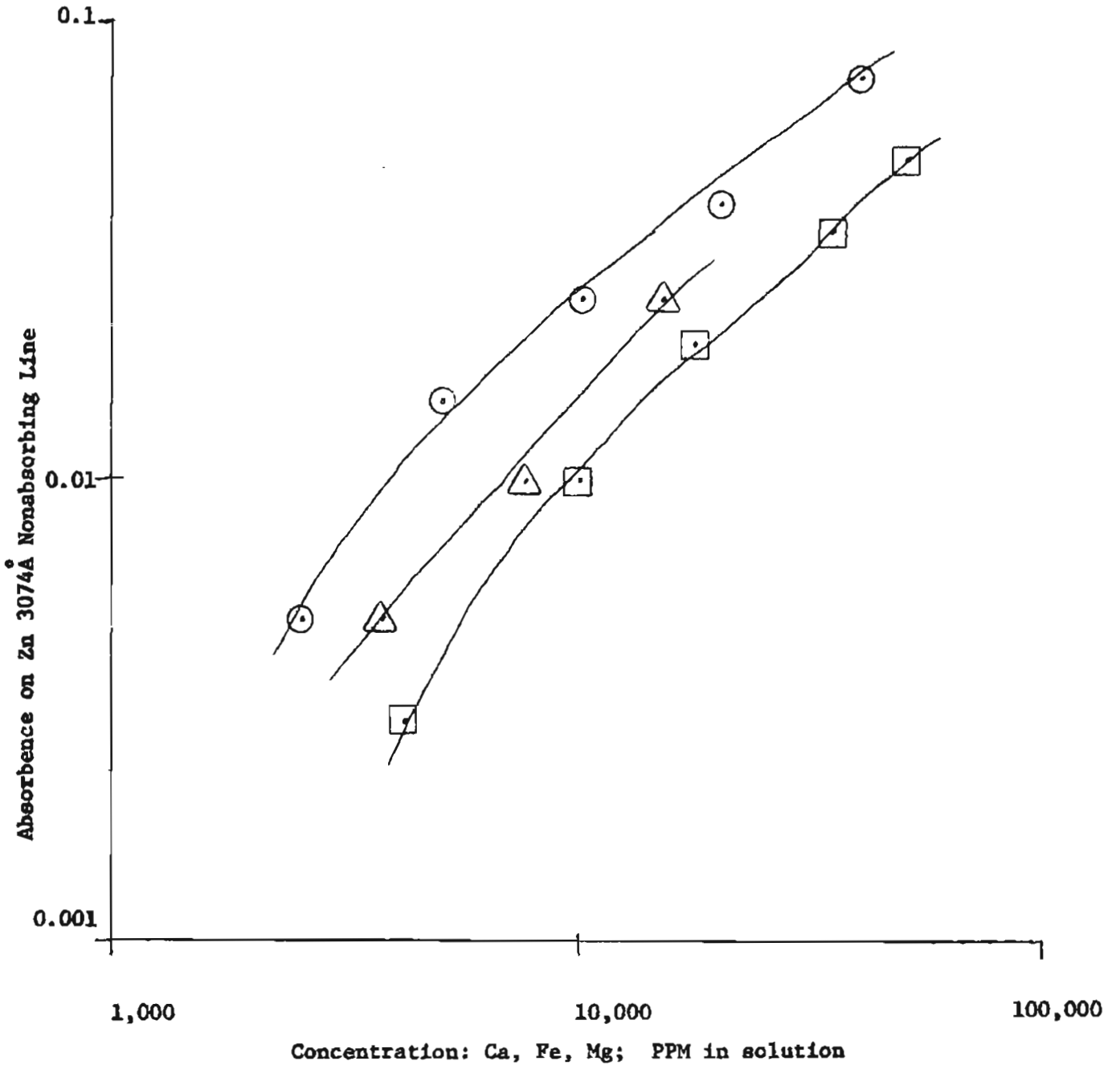


FIGURE 1. Absorbance vs. concentration of Ca, Mg and Fe on the 3074Å Zn line.

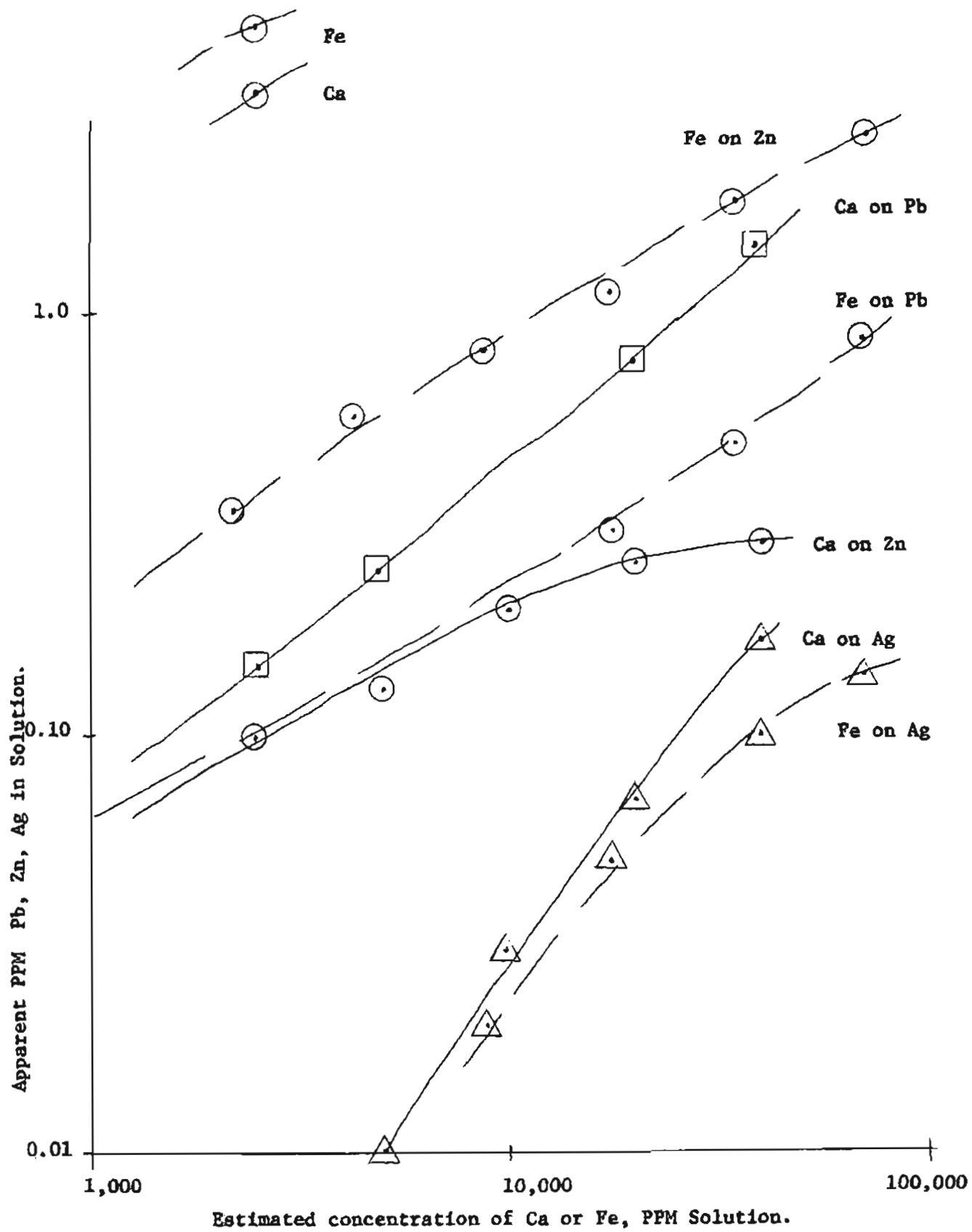


FIGURE 2. Correction for interference of Ca and Fe on Pb, Zn and Ag.

Table 2
MINIMUM LEVEL OF SIGNIFICANT INTERFERENCE

INTERFERING ELEMENT	CONCENTRATION IN SOLUTION	WT% SOLUBLE* IN SAMPLE	WT% SOLUBLE** MINERAL	LEVEL OF INTERFERENCE
Fe	20,000	20%	26% hematite	for Zn, 14 ppm
Fe	20,000	20%	26% hematite	for Pb, 3.5 ppm
Fe	5,000	5%	6.5 hematite	for Ag, 0.1 ppm
Ca and Mg	-----	---	-----	for Zn, correction is not necessary; 100% calcite indicates 3 ppm Zn
Ca and Mg	10,000	10%	16% calcite	for Pb, 4.6 ppm
Ca and Mg	5,000	5%	8% calcite	for Ag, 0.1 ppm

* This column means the weight per cent of the element in the sample that is soluble in hot aqua regia.

** This column states the weight per cent of hematite or calcite in the sample that would give high enough iron or calcium to interfere "significantly".

R E F E R E N C E S C I T E D

Billings, Gale, K., 1965, Light Scattering in Trace-Element Analysis by Atomic Absorption: Atomic Absorption Newsletter, p 357-61

Capacho-Delgado, Luis, and Sprague, Sabina, 1965, Calcium Interference in Atomic Absorption Analysis for Barium: Atomic Absorption Newsletter, p 363-64.

Slavin, Walter, 1965, Comments on "Light Scattering in Trace-Element Analysis". Atomic Absorption Newsletter, p 361-62