

REFORMULATION OF SPECTROMETRIC STANDARDS USING AQUEOUS RAW MATERIALS

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14. ABSTRACT Rotrode atomic emission spectrometry is used by all three military oil analysis programs to determine wear debris in engine oil. Instruments are calibrated and standardized with a series of chemical standards that are significant expenditures for the program. Raw materials contribute the most to the cost of the end product. Less expensive commercially available aqueous (rather than oleic) products were explored as raw materials. Aqueous formulation was shown to be unfeasible, but water-in-oil emulsions had similar savings. Emulsions also performed similarly to oleic standards in several regards. Differences in matrix effects observed on different spectrometers confound the implementation and preclude a seamless integration of an alternative matrix. Some uses of emulsion-based standards were validated, but further developmental work is required prior to use in a field laboratory.					
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Reformulation of spectrometric standards using aqueous raw materials

Executive summary

Rotrode atomic emission spectrometry is used by all three military oil analysis programs to determine wear debris in certain platforms. These instruments are calibrated and standardized with a series of chemical standards that have continually increased in cost over the years, becoming a significant portion of the expenditures for the overall program. The organic raw materials that are the sources of the analytes (elements) and that are used in the manufacture of these chemical standards contribute the most to the cost of the end product. In order to try to reduce costs associated with manufacturing, an effort was undertaken to explore relatively less expensive commercially available aqueous (rather than oleic) products for use as raw materials. While a completely aqueous chemical standard was shown to be unfeasible, water-in-oil emulsions with cost savings on the same order of totally aqueous products were found to be easily made and to give similar performance to oleic standards on any specific instrument. Nevertheless, differences in matrix effects observed on different rotrode atomic emission spectrometers confounded the implementation and suggested that the spectrometer manufacturer's accuracy and precision specifications were set so as to allow for the variability in signal that results from matrix effects. Moreover, these differences among the instruments' responses to the water-in-oil emulsive matrix and the oleic matrix relative to one another preclude a seamless integration of an alternative matrix. On the other hand, some uses of emulsion-based standards were validated, but further developmental work would be required prior to actual use in a field laboratory.

I. Background

The three military oil analysis programs (Navy, Army, Air Force) rely on rotrode atomic emission spectrometry for the qualitative and quantitative determination of microscopic metallic wear debris (e.g., Fe, Ti, Pb, Ag, Cu, Al, inter alia), metal compound additives (e.g., Zn, Mo) and some nonmetallic compounds found as contaminants or additives (i.e., B, Na, Si). Rotrode spectroscopy relies on an AC arc for atomization, ionization, and excitation of the species present in the oil. Rotrode arc spectroscopy suffers from a number of limitations. Chief among these are the low energy available for electronic promotion, substantial impact from matrix effects, and the reproducibility of nebulization/excitation. One of the principal consequences of the low energy is that calibration curves tend to be nonlinear and linear dynamic ranges tend not to extend over more than about two orders of magnitude. However, it finds favor in military applications due to the relative ruggedness of the instruments, minimal operator training requirements, longevity and stability of consumable supplies (disks and rods), low waste stream, and low facility needs (no specialized power constraints, modest climate controls).

Historically, the rotrode spectrometers have been calibrated at the factory with a 19-element standard made in SAE 50 oil. In the field, the units are standardized to account for various factors that can elevate or attenuate the signal without regard to cause. In this report, the distinction between *standardization* and *calibration* will be kept in a manner consistent with the usage of these terms by the current primary instrument maker (Spectro, Inc.). Specifically, calibration refers to the relationship between hydrogen-normalized intensity and the concentration of analyte. Standardization refers to a linear correction performed when the operator initiates a procedure that examines the hydrogen-normalized intensity at 100 ppm and in the blank. In practice, the units are calibrated infrequently and standardized routinely.

The spectrometers rely on a piecewise function made of linear segments fixed by the calibration points. The instrument first acquired by the military in bulk, the A/E35U-3, apparently was calibrated with a mixture of standards (Rhine, 1983). Calibration was performed with the following chemical standards: Ag, Cr, Ni, Al: 10, 20, 50, 60 ppm; Cu: 10, 20, 30, 50 ppm; Fe: 10, 20, 25, 40, 50, 60, 75, 100 ppm; Mg: 10, 20, 40, 60, 100 ppm; Ti: 10, 20, 50, 100 ppm; Si: 5, 10, 20 ppm (Rhine, 1983). Somewhat curiously, none of the calibration curves shows a response for a blank (0 ppm). It is assumed that more points were used for iron because of its importance and prevalence over other metals, especially in earlier equipment. At the time, calibration curves were prepared in a variety of matrixes; the response for iron was demonstrably nonlinear in MIL-L-7808, and this may also explain the larger number of points. For all analytes except perhaps Si, the calibration curves were most nearly linear or indistinguishable from linear in Conostan 245, which is also available as NIST SRM 1083, although the sensitivity is also the lowest in Conostan 245. Regardless, the investigators were well aware of the matrix effects at the time. A subsequently report argued for the value of what the authors termed the spark-in-vapor method (SIVM) over rotrode spectrometers due to matrix-invariance (Rhine, 1985). The authors seem to suggest that it would have been desirable to retrofit the extant A/E35U-1 and A/E35U-3 with SIVM technology to reduce the impact of the

matrixes on the results. Other investigations have dissolved wear debris in oxidizing acids, chelated the metal cations, and then redissolved the complexes into an oleic matrix (Swanson, 1995). A mixture of 8-quinolinol, ammonium pyrrolidinedithiocarbamate, and ammonium *N, N'*-diethyldithiocarbamate were used to solubilize the metal cations in base oil. 8-Quinolinol is well-known for its ability to complex with aluminum(III) and other Pearson hard acid metal cations, while dithiocarbamates preferentially complex with the softer acid cations, such as mercury(II). When softer Lewis acid metal ions are not present, dithiocarbamates will also complex with the harder metal acids. All of these complexants are used as metal extractants and can be used as phase-transfer agents to solubilize metal cations in organic solvents. Normally, low viscosity solvents are used for the extraction, e.g., methyl isobutyl ketone, chloroform, methylene chloride, or methyl *t*-butyl ether, but Swanson was attempting to extract the metal cations into a mineral oil matrix directly. One of the problems with using these complexants is that they can also serve as lipophilic detergents, aiding in either dispersing water into the oleic matrix or partial emulsification, which can be linked to localized sludge formation and changes in physical properties (increased heat capacity, increased viscosity, changes in background spectrum). Swanson attempted to minimize this by keeping the ionic strength and concentrations of hydrophilic neutral inorganic species (e.g., NH_3) of the aqueous phase high. In general, reverse micelle formation does not occur, because of the carbon chain length and the molecular geometry. Overall, it can be concluded that the process of acid-digestion, solubilization, and redissolution of the metallic species into an oleic matrix is unnecessarily complicated, reduces precision in the results, and should be avoided for wear debris itself. On the other hand, it can be inferred from Swanson's work that—when the debris itself is in the oleic matrix—forcing aqueous inorganic standards into the oleic phase is both reasonable and achievable.

In most instruments, the concentrations used for calibration follow the D19 series of standards manufactured by the JOAP TSC: 0, 5, 10, 30, 50, 100, 300, 500, 700, 900 ppm; nevertheless, there is no formalized calibration procedure set by any cognizant authority. That notwithstanding, the TSC provided only those concentrations listed above to the instrument makers, and it tested instrument performance on those concentrations (as well as the equivalent D12 series and D3-100) during evaluations against the commercial instrument description (CID) (Poff, 1999a, b). It is reasonable to infer that calibration curves based on these 10 concentration values were anticipated to meet the CID requirements.

Because some of the analytes are decidedly nonlinear in response, performance of piecewise linear functions can be inadequate—especially near 100 ppm—since the sensitivity (i.e., slope) on the interval [50, 100 ppm] is substantially different from that on the interval [100, 300 ppm]. As a result, the manufacturer has adopted a practice of inserting intermediate values to help to smooth out the curve, generating artificial piecewise functions, especially near 75-80 ppm and near 120-125 ppm. The insertion of two or more points in these regions dramatically reduces the time required for standardization, but the data used are fictitious because they are not based on the responses of analytical standards at these concentrations. Occasionally, field technicians insert additional fictitious values, depending on the performance of the instrument. This practice has become widespread and is generally accepted now by the program offices as well as the various technicians as a workaround for a software limitation. The Spectro instrument met the performance criteria at the time of CID-

testing (Poff, 1999a). Although the CID test report for the Spectroil M/N does not say whether any fictitious points were inserted into the calibration curves of the test instrument (Poff, 1999a), TSC staff present at the time indicate that all calibrations were observed and that only real data obtained from the D19 series were used (Humphrey, 2005).

In addition to the D19 series, the JOAP TSC manufactures a D12 series and D3-100 (100-ppm equivalent response to D19-100). The D12 series is manufactured at the same concentrations as the D19 series, but is intended to be used for standardization only. The D12 series is manufactured to less stringent specifications and has a lifetime that permits some degradative loss, especially under uncontrolled field storage conditions. The D12 series is intended to be used for standardization only, and individual standards are to be replaced if standardization factors show substantial increases or decreases, data acquired on the D12 standards are erratic, visible degradation has occurred, or certification testing suggests poor instrument performance.

The chemical sources of the analytes are purchased on a per gram cost basis (as the element). Over the past two years, the raw material cost has fluctuated near the \$100 per gram mark, but has previously escalated to over \$200 per gram. The D19 series has a shelf life of one year under optimal conditions, while the D12 series has a shelf life of 30 months under optimal conditions. In order to maintain adequate reserves, there is a continual loss of inventory (and concomitant cost) associated with expired D12 and D19 standards. Therefore, any modifications that could lower raw material costs, increase lifetime, or both, were viewed as attractive areas for applied research.

The chemical sources of the current D12, D19, and D3 standards are a mixture of oil-miscible and oil-soluble compounds, some of which are considerably expensive to synthesize, purify, and dissolve in appropriate solvents. In many cases, these solvents are inconvenient to work with because of their disparate rheophysical properties. The varying solubilities of the raw materials in mixed solvents also affects the manufacturing process due to the potential for precipitation or cross-reaction as the reagents are combined, but prior to being well-mixed. Because the primary degradative processes are oxidative or hydrolytic, moving to a highly stable series of inorganic salts in acidic aqueous solution was viewed as highly desirable. In addition, there are considerable cost savings to be realized in moving from an oleic solution to an aqueous solution, on the order of a 60-70% decrease in the end product cost, depending on the concentration.

II. Aqueous solutions

Preparation of stock. A 500 ppm aqueous solution was prepared from 10,000 ppm commercial standards. The commercial products contain ~5% w/w nitric acid. The titanium solution is stabilized with a trace of HF. The 500-ppm solution showed no signs of degradation when further acidified with perchloric acid. Despite the fact that some of the salts are expected to be incompatible and lead to precipitation of insoluble molybdates, vanadates, or borates, no such reaction was observed over a period of months when stored in 0.5% w/w perchloric acid.

Rheological modifiers. Attempts to increase the viscosity via the use of various polymeric thickening agents (e.g., Alcogum) showed poor results. Although some of these materials are designed to withstand acidic media (e.g., hydrochloric acid-based toilet cleaners), the manufacturers caution against using their products in the oxidizing environment of nitric acid solutions. Substantial denaturation and flocculation were observed. All of the rheological modifiers that were tested were found to be insufficiently stable in a nitric acid environment.

Surface tension. An additional problem with the aqueous solutions is a consequence of the high surface tension of the aqueous solution, which resists shearing by the rotating disk. Instead, the highly cohesive liquid phase avoids wetting the the surface of the disk without the addition of a surfactant. This complicates the sampling process. In other words, it is difficult to reproducibly coat the disk with a layer of aqueous solution. This leads to imprecision and variable response related to the height of the liquid in the sample container.

Aberrant tin readings. The difference in conductivity and heat capacity of the aqueous matrix also appear to affect the arc in a way that is not easily accounted for and that interferes with the measurement of tin. Tin is monitored by following the emission at 317.502 nm, which corresponds to a transition of the Sn^{I} cation. Unfortunately, the arc spectrum is sufficiently changed that even the water blank shows a signal at this wavelength for a nonzero concentration. Various attempts to modify the matrix were unsuccessful in eliminating this emission band. Essentially, the signal associated with the blank was such that the detection limit was raised to an unsatisfactorily high level. Although there is no tin in the material, the spectrometer identifies this elevated signal as tin in the sample. This problem is essentially impossible to work around because the actual samples will be in oleic solution and not aqueous solution. Therefore, oleic blanks would actually appear to have negative tin concentrations, and oleic solutions with several ppm of tin could actually appear to have none. This phenomenon in particular indicated that a non-oleic medium would not be successful. The phenomenon appears to be wavelength dependent and most severe near 317.5 nm. It is unclear what physicochemical factors are primarily responsible, but dielectric constant and heat capacity are speculated to be involved.

III. Water-in-oil emulsions

Emulsion composition. The various problems with formulations containing no oil suggested that a smooth transition would be highly unlikely. Consequently, the research moved towards emulsions that contained oil as a significant component. A series of trial experiments showed that reasonably stable emulsions (separating over days) could be prepared using nonylphenol ethoxylates, specifically, those with 4, 6, and/or 9 moles of ethylene oxide per mole of nonylphenol. Hereafter, these will be designated as NP4, NP6, and NP9, respectively. No degradation to the surfactants was evident from the high acid concentration. NP4 is immiscible in water (hydrophobic) and miscible in SAE 50. NP9 is readily miscible in water (hydrophilic); it is somewhat soluble in SAE 50. Three different oils were tested: SAE 50 base stock, light mineral oil, and heavy mineral oil. Both of the mineral oils are designated as white (colorless).

Foaming and emulsification. Although some foaming is evident during vigorous rotation or shaking, the foam is unstable and collapses quickly, probably due to the high ionic strength of the aqueous phase and the carbon chain length of the oleic compounds. Multiple tests of emulsions immediately after vigorous mixing demonstrated imprecision consistent with that of the instrument; variation in reproducibility could not be associated with foaming. In addition, the pre-burn part of the analytical cycle heats the sample, which results in rapid and virtually complete collapse of the foam. After mixing, the emulsifications separated substantially over 2-3 days; no separation was evident within 2 hours of initial mixing. Additional mixing after separation of the phases rapidly led to re-emulsification. No degradation (e.g., gelling) was evident over a period of several weeks for the best-performing emulsions. Emulsions based on NP6 alone or combined with either NP4 or NP9 performed poorly. Combinations of NP6 and NP9 performed best; addition of the lipophilic NP4 did not appear to further enhance performance. Emulsion formulation 7 seemed to have satisfactory properties in terms of speed of emulsification, time to separation, and foaming. Emulsion formulation 7 was composed of the following (w/w): 1.0% NP6, 1.0% NP9, 20% aqueous solution, and 78% SAE 50. The water content was fixed at 20% w/w regardless of the analyte concentrations and volume of 500-ppm stock solution; the balance of the water content was made up with deionized water. Emulsion quality declined when the concentration of either surfactant was reduced. Increasing either surfactant concentration increased foaming, and did not seem to improve emulsion quality meaningfully, so it was abandoned from a cost-savings perspective. Likewise, tests with mineral oils in place of SAE 50 did not seem to have any benefit. In fact, the incorporation of white mineral oils led to rather volatile emulsions that tended to evaporate, boil, and/or ignite when exposed to the arc.

Data collection. Four rotrode spectrometers (0532, 0786, 0794, 0620) were standardized with R205 reference standard and check burns were performed. Data were collected for five burns of solutions (emulsion formulation 7) made at four different concentrations: 5, 10, 50, and 100 ppm. At the same time, data were collected for five burns of reference standard R205 at the same concentrations. Although the emulsion formulation contained all D19 analytes, only the D12 and D3 analytes were examined, in part because three of the spectrometers used for testing were set up only for the D12 and D3 series. The D12 series includes the following: Fe, Ag, Al, Cr, Cu, Mg, Na, Ni, Pb, Si, Sn, and Ti; D3 includes B, Mo, and Zn. All data were collected in concentration mode (see Table 1).

IV. Analysis, results, and discussion

Quintuplicate analyses were used for all calculations. The emulsion formulation 7 data were normalized (ratioed) to the R205 data and then equated (multiplied by) the nominal values. In general, attenuation of the signal is observed as a result of the emulsion matrix as Table 2 shows. Nine of twelve elements showed attenuation on the order of 20% in the emulsion relative to the D19 response in oil. In other words, reported concentrations are about 20% low. In many cases, the signal is attenuated more with increasing concentration. Several elements show heightened response at 5 ppm in the emulsion relative to oil. Silver, lead, tin, and molybdenum have normalized intensities 20-30% higher than R205. Silicon is exceptional in that it responds almost identically at 5 ppm regardless of the matrix; however, it has only 76% of the response of R205 at 100 ppm.

Experiments performed on four different spectrometers demonstrated that a strictly increasing function (intensity versus concentration) was obtained. Unfortunately, there can be large differences in sensitivity between an oleic matrix and an emulsive matrix. Iron will be considered here because of its linearity. Relative sensitivity of unity means that the instrument response is identical regardless of matrix. One spectrometer had a relative sensitivity of 0.65 for Fe, while another had a relative sensitivity of 0.85. It seems that the difference in sensitivity carries over to other elements. In other words, some spectrometers seem to respond less to the emulsion than others do relative to how they respond in oil. This would seem to indicate overall lower volatility, ionization, or some other instrument-dependent bias. Such biases could be corrected for computationally, but not with the current software.

The normalized values are sorted in Table 3 by concentration and then spectrometer for easy comparison by inspection. One of the curiosities of this table is that the spectrometers show a correlation between spectrometer number and signal intensity; however, this probably does not suggest any real relationship between the two quantities. Rather, it shows that individual spectrometers tend to report higher or lower across the board and suggests that matrix effects can be accounted for via either a computational correction or a chemical correction (i.e., a shift in the actual analyte concentration). Spectrometer 0795 actually shows a higher response in the emulsion than it does in the oleic matrix for several elements. The importance of the matrix was recognized as early as 1983 (Rhine, 1983). Matrix effects have consequences not only for the implementation of alternate matrixes for calibration and/or standardization standards, but also for improving the quality of measurements in different kinds of lubricating or hydraulic fluids (e.g., MIL-L-23699, MIL-L-2104, MIL-H-5606, MIL-H-83282; note that these are technically all MIL-PRF documents). Furthermore, it may be possible to separate spectrometers into bins, such as deciles, quintiles, or terciles. It is altogether possible that a physical component, such as the arc source, is responsible for this type of phenomenon. Figure 1 illustrates these trends for Fe, Ag, Al, and Cr. The behavior from element to element is quite similar among these five spectrometers. An alternative way of demonstrating the trends is to plot a calibration curve for each element and to compare the results from the various spectrometers; Figures 2-4 show the trends for Fe, Ag, and Al, respectively.

It is possible that the manufacturer was aware of the matrix-associated differences in reported concentration and made use of such knowledge in constructing the “acceptable accuracy indices,” which would conventionally be viewed as determinate (absolute) error. If one looks at the coefficients of variation (relative standard deviations) and compares these to allowable relative error (ratio of acceptable accuracy index to nominal concentration), one finds that the range of values for the the 10 ppm standard in emulsion is within the limits for all 15 elements. Although 28 of 60 values do not meet the manufacturer’s accuracy limit when analyzed in this way, only 11 of 60 values exceed the limits by more than 5%, which is unsurprising given the small sample tested (five spectrometers). Therefore, it seems reasonable to infer that fundamental differences between spectrometers have resulted in wide latitude for the performance specifications. In other words, the tolerances appear to be quite high, and the rather poor specifications in the manual appear to be intended to address the differences among instruments. In actual practice, individual spectrometers can be maintained sufficiently well so as to sustain a performance far superior to what the

manufacturer guarantees in its manuals. Exceedance of the manual's limits is well-documented by the performance on the petroleum-based certifications standards (usually #1 and #2). In fact, even on the synthetic oil (#3 and #4), which is similar to MIL-L-23699, we find performance that exceeds the manual's limits. Accordingly, the large allowances in variability would appear to have been established primarily to address matrix differences and to meet minimalist requirements for calibration, namely, the use of a single series of calibration standards in a single matrix. It appears that a decision was made to trade precision and accuracy for the ease in manufacturing (perhaps justified in terms of development cost savings). Given Rhine's results (1983) on the A/E35U-3, we must conclude that the program managers were aware of and accepted biased performance in other matrixes. None of the previous studies could have determined the nature of the bias since the investigators appear to have had access to only one instrument at any time. For whatever reason, the program managers did not opt to tighten the instrument performance requirements even in the matching matrix (i.e., SAE 50 mineral oil). Unfortunately, the consequence of that decision is a fleet of instruments sufficiently dissimilar to prevent the adoption of an alternative matrix for chemical standards. The large permissible errors (inaccuracy and/or imprecision) have also led to a certification program whose criteria for passing permits wide variation so long as a significant subset of instruments are not tightly aligned. In other words, varying biases from spectrometer to spectrometer in moving between the two matrixes appear as a large fleetwide imprecision, indicated by relatively larger population standard deviations and standard errors as contrasted with the performance in SAE 50 mineral oil.

Overall, the data obtained thus far suggest that it will not be possible to seamlessly replace D12 or D3 series products with emulsion series products, named as "E12" or the respective number hereafter. Nevertheless, the data do suggest that one could use a series of emulsion products for checks, but that the expected values would have to be obtained from an operationally defined empirical instrumental response for a particular emulsion. In addition, the data suggest that it would not be possible to abandon the D19 series in oleic solution. An E19, E15, or E12 series could be developed that incorporates all current concentrations as well as additional concentrations. The aqueous phase would have a virtually limitless shelf-life. The surfactants and oil could be packaged separately from the aqueous phase. The contents of the aqueous phase could be packaged in a sealed vial and added by the end user, thus beginning the lifetime countdown.

The empirical relationship would be obtained by a procedure carried out by the end-user or a service technician. First, a newly D19-calibrated spectrometer would be standardized using the D19 series. Then, the E-series standards would be burned in quintuplicate to determine their expected values. These expected values would be used to change the set points for standardization. The ability to change the concentration used for the standardization calculation already exists within the current software, so this is a minor operational consideration. Because the emulsion tends to attenuate the signal at 100 ppm, this would tend to produce apparent concentrations near 70-80 ppm being used for standardization, which are nicely bracketed by the 50 and 100 ppm intensity ratio data. Because the attenuation or augmentation is on the order of 20-30%, the extant D12 concentrations would suffice to construct E12 (or E15, E19, etc.) concentrations for check burns. Such a process would

require further development and validation and would reflect a number of substantial changes in how the instruments are set up and used.

The time required for this process would be on the order of 16 person hours total. Assuming an operator hourly rate on the order of \$25 equates to \$400 in labor costs. If the average laboratory goes through six bottles of product yearly with an average cost of \$200 per bottle, that is \$1200 spent on supplies. The projected cost savings is at least 60%, so that would equate to a net savings of \$720 the first year. However, it would be necessary to track the process. Software development would also increase costs. Regardless, a complete return would be anticipated within a few years.

There remain several unresolved issues which would require further work before any validation could take place. Although the acid content of the emulsion products is lower than toilet bowl cleaner, degradation of some of the metal components of the instrument could be realized with extended use, especially if cleaning is inadequate. This would have to be more carefully investigated. In addition, the long-term stability of the products has not been explored sufficiently. Although separation and re-emulsification occur over the short term, the long-term reversibility has not been studied. Only if there is willingness to accept the implementation issues should these studies be performed.

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Table 1. Concentration data for emulsion formulation 7, R205 reference standard, and a linearly normalized value for the D12 and D3 elements (nominal concentration is given in the column labeled c/ppm)

matl	spec	c/ppm	Fe	Ag	Al	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	B	Mo	Zn
E7	0795	5	3.2	6.7	3.3	3.6	4.4	2.8	5	3.6	5.3	3.2	3.9	4.4	2.8	8	4.9
E7	0795	10	5.9	13.2	6.6	6.7	7.2	5.1	9.2	6.6	10.4	5.8	7.3	7.1	5	14.9	8
E7	0795	50	45	78.5	50.4	47.4	56.6	47.1	53.5	46.9	57	28.2	54	45.5	33.8	63	50.4
E7	0795	100	99.1	168	109	99.9	116	107	106	100	128	66.9	115	101	78.7	123	133
R205	0795	5	3.6	5.4	3.6	4.4	4.5	3.2	4.1	4.2	4.1	3	3	5.1	4.9	6	5.2
R205	0795	10	7.5	9.3	9.8	8.8	8	7.1	9.8	8.2	7.7	7.5	6.5	9.2	8.5	11.2	9.5
R205	0795	50	48.4	53.9	50.7	50	49	48.8	49.7	47.7	48.4	46.4	48.7	51.4	52.5	56.5	51.1
R205	0795	100	99.7	107	99.7	98.3	97.5	102	94.6	97.1	101	99.6	100	102	100	102	101
Norm	0795	5	4.44	6.20	4.58	4.09	4.89	4.38	6.10	4.29	6.46	5.33	6.50	4.31	2.86	6.67	4.71
Norm	0795	10	7.87	14.19	6.73	7.61	9.00	7.18	9.39	8.05	13.51	7.73	11.23	7.72	5.88	13.30	8.42
Norm	0795	50	46.49	72.82	49.70	47.40	57.76	48.26	53.82	49.16	58.88	30.39	55.44	44.26	32.19	55.75	49.32
Norm	0795	100	99.40	157.01	109.33	101.63	118.97	104.90	112.05	102.99	126.73	67.17	115.00	99.02	78.70	120.59	131.68
E7	0786	5	4.10	7.30	3.70	4.30	5.10	3.20	5.30	3.60	6.70	5.20	5.60	4.20	3.60	5.90	4.40
E7	0786	10	7.20	13.60	7.30	7.60	8.00	6.10	11.60	6.90	11.10	8.80	10.00	6.90	6.70	10.60	7.30
E7	0786	50	41.10	61.40	43.00	41.60	47.20	40.50	48.30	40.80	48.80	45.60	46.30	36.80	38.70	49.20	42.90
E7	0786	100	84.00	115.00	92.40	87.40	91.40	86.60	98.50	85.70	102.00	94.50	95.20	81.00	82.60	102.00	121.00
R205	0786	5	4.80	5.90	4.20	5.10	5.30	3.90	4.40	4.30	4.50	4.70	3.90	5.30	5.10	4.50	4.80
R205	0786	10	9.60	9.70	8.60	9.30	8.90	9.00	10.90	8.50	8.90	9.30	9.20	9.30	9.60	9.40	9.30
R205	0786	50	57.10	59.20	53.10	52.00	56.10	56.70	50.70	51.30	53.70	54.30	53.60	55.30	57.40	57.40	62.40
R205	0786	100	107.00	112.00	105.00	104.00	110.00	106.00	108.00	105.00	105.00	106.00	104.00	105.00	107.00	107.00	108.00
Norm	0786	5	4.27	6.19	4.40	4.22	4.81	4.10	6.02	4.19	7.44	5.53	7.18	3.96	3.53	6.56	4.58
Norm	0786	10	7.50	14.02	8.49	8.17	8.99	6.78	10.64	8.12	12.47	9.46	10.87	7.42	6.98	11.28	7.85
Norm	0786	50	35.99	51.86	40.49	40.00	42.07	35.71	47.63	39.77	45.44	41.99	43.19	33.27	33.71	42.86	34.38
Norm	0786	100	78.50	102.68	88.00	84.04	83.09	81.70	91.20	81.62	97.14	89.15	91.54	77.14	77.20	95.33	112.04

Table 1 continued

matl	spec	c/ppm	Fe	Ag	Al	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	B	Mo	Zn
E7	0532	5	2.60	6.10	2.70	3.10	3.10	2.00	4.90	2.60	6.10	3.80	5.00	2.50	3.20	6.00	4.00
E7	0532	10	5.10	10.40	5.40	5.80	5.70	3.90	8.80	5.30	8.50	6.70	7.40	5.30	6.20	10.70	7.20
E7	0532	50	31.80	45.90	32.80	34.30	34.50	31.70	42.90	33.70	39.40	36.10	37.30	30.90	35.00	47.20	47.30
E7	0532	100	66.10	78.90	70.40	72.10	66.90	68.00	78.80	68.40	81.60	73.40	76.00	67.10	78.30	92.30	104.00
R205	0532	5	4.70	5.40	4.30	5.00	4.90	3.50	4.90	4.40	4.40	4.30	4.20	4.90	5.50	5.80	6.10
R205	0532	10	9.20	8.90	8.20	9.40	8.40	7.60	9.70	8.80	8.20	8.90	9.30	9.70	9.80	11.60	11.70
R205	0532	50	50.90	51.00	51.60	52.30	49.00	50.80	52.90	48.60	49.40	49.20	49.20	49.90	52.40	53.90	63.80
R205	0532	100	98.10	102.00	102.00	104.00	99.00	97.00	105.00	102.00	101.00	99.90	101.00	97.90	104.00	103.00	102.00
Norm	0532	5	2.77	5.65	3.14	3.10	3.16	2.86	5.00	2.95	6.93	4.42	5.95	2.55	2.91	5.17	3.28
Norm	0532	10	5.54	11.69	6.59	6.17	6.79	5.13	9.07	6.02	10.37	7.53	7.96	5.46	6.33	9.22	6.15
Norm	0532	50	31.24	45.00	31.78	32.79	35.20	31.20	40.55	34.67	39.88	36.69	37.91	30.96	33.40	43.78	37.07
Norm	0532	100	67.38	77.35	69.02	69.33	67.58	70.10	75.05	67.06	80.79	73.47	75.25	68.54	75.29	89.61	101.96
E7	0620	5	2.60	5.80	3.10	2.90	3.10	2.80	4.00	2.60	3.70	4.60	5.70	2.60	2.70	3.50	3.00
E7	0620	10	5.70	12.90	6.30	6.50	6.70	6.70	7.50	6.00	7.10	7.10	8.80	6.20	4.40	6.60	6.70
E7	0620	50	33.30	42.40	37.50	35.90	35.70	35.60	42.50	33.90	42.40	38.60	37.20	31.30	35.90	38.90	33.70
E7	0620	100	64.50	64.50	69.50	68.80	57.80	64.40	68.90	63.40	76.30	70.90	71.30	60.70	69.00	76.20	100.40
R205	0620	5	4.70	5.10	4.90	4.90	5.00	5.30	4.60	4.50	4.60	5.50	5.90	5.50	4.50	4.80	4.90
R205	0620	10	8.70	9.20	8.50	8.60	8.80	9.70	8.40	8.20	8.30	10.50	8.70	9.90	8.30	8.10	8.60
R205	0620	50	50.10	48.20	48.10	49.10	47.00	48.00	50.30	45.50	49.80	49.40	46.30	47.90	48.10	48.70	47.00
R205	0620	100	102.00	101.00	103.00	99.00	100.00	100.00	96.90	99.00	100.00	101.00	101.00	102.00	99.00	102.00	102.00
Norm	0620	5	2.77	5.69	3.16	2.96	3.10	2.64	4.35	2.89	4.02	4.18	4.83	2.36	3.00	3.65	3.06
Norm	0620	10	6.55	14.02	7.41	7.56	7.61	6.91	8.93	7.32	8.55	6.76	10.11	6.26	5.30	8.15	7.79
Norm	0620	50	33.23	43.98	38.98	36.56	37.98	37.08	42.25	37.25	42.57	39.07	40.17	32.67	37.32	39.94	35.85
Norm	0620	100	63.24	63.86	67.48	69.49	57.80	64.40	71.10	64.04	76.30	70.20	70.59	59.51	69.70	74.71	98.43

Table 1 continued

matl	spec	c/ppm	Fe	Ag	Al	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	B	Mo	Zn
E7	0794	5	7.60	10.30	6.10	5.40	7.10	6.80	3.40	6.20	8.30	8.80	17.70	7.60	4.30	10.10	8.60
E7	0794	10	6.20	11.30	6.40	5.80	6.10	5.10	7.20	5.80	7.00	7.10	8.50	5.40	4.90	7.60	4.80
E7	0794	50	41.00	57.10	46.20	42.70	48.70	41.20	48.10	41.90	51.80	37.40	46.60	38.00	38.10	47.80	43.40
E7	0794	100	85.90	102.10	95.00	89.80	90.20	86.70	92.60	89.30	103.20	79.60	95.80	82.60	82.30	100.90	108.10
R205	0794	5	6.30	6.20	5.90	5.80	6.10	5.40	5.10	6.10	6.10	6.10	6.20	6.10	5.80	6.10	5.40
R205	0794	10	8.00	8.80	7.90	8.40	8.50	7.40	7.80	8.30	7.90	8.20	8.80	8.30	8.00	8.30	8.00
R205	0794	50	46.70	48.40	46.90	47.90	47.50	45.20	47.60	45.30	47.20	47.00	45.70	46.50	48.10	47.60	50.40
R205	0794	100	100.00	101.00	101.00	101.00	101.00	100.00	103.00	102.00	101.00	101.00	100.00	101.00	100.30	102.00	105.00
Norm	0794	5	6.03	8.31	5.17	4.66	5.82	6.30	3.33	5.08	6.80	7.21	14.27	6.23	3.71	8.28	7.96
Norm	0794	10	7.75	12.84	8.10	6.90	7.18	6.89	9.23	6.99	8.86	8.66	9.66	6.51	6.13	9.16	6.00
Norm	0794	50	43.90	58.99	49.25	44.57	51.26	45.58	50.53	46.25	54.87	39.79	50.98	40.86	39.60	50.21	43.06
Norm	0794	100	85.90	101.09	94.06	88.91	89.31	86.70	89.90	87.55	102.18	78.81	95.80	81.78	82.05	98.92	102.95

Notes: E7 = emulsion formulation 7, R205 = reference standard, normalized value = (nominal concentration) × (value for EF 7) ÷ (value for R205)

Table 2. Summary statistics for normalized emulsion formulation 7 on 5 spectrometers for D12 and D3 series elements

stat	c/ppm	Fe	Ag	Al	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	B	Mo	Zn
avg	5	4.06	6.41	4.09	3.80	4.36	4.05	4.96	3.88	6.33	5.34	7.75	3.88	3.20	6.06	4.72
avg	10	7.04	13.35	7.46	7.28	7.91	6.58	9.45	7.30	10.75	8.03	9.97	6.67	6.12	10.22	7.24
avg	50	38.17	54.53	42.04	40.26	44.85	39.57	46.96	41.42	48.33	37.58	45.54	36.41	35.24	46.51	39.93
avg	100	78.88	100.40	85.58	82.68	83.35	81.56	87.86	80.65	96.63	75.76	89.64	77.20	76.59	95.83	109.41
esd	5	1.36	1.09	0.90	0.74	1.19	1.46	1.17	0.94	1.34	1.20	3.75	1.56	0.39	1.74	1.96
esd	10	0.98	1.08	0.83	0.77	1.03	0.82	0.69	0.86	2.19	1.05	1.28	0.91	0.61	2.06	1.09
esd	50	6.69	11.87	7.55	5.90	9.43	7.12	5.56	6.10	8.17	4.45	7.42	5.81	3.10	6.38	6.20
esd	100	14.56	35.62	17.63	13.71	23.49	15.79	16.17	15.87	20.01	8.64	17.71	14.87	4.58	16.64	13.42
att	5	0.811	1.281	0.818	0.761	0.871	0.811	0.992	0.776	1.267	1.067	1.549	0.777	0.640	1.213	0.944
att	10	0.704	1.335	0.746	0.728	0.791	0.658	0.945	0.730	1.075	0.803	0.997	0.667	0.612	1.022	0.724
att	50	0.763	1.091	0.841	0.805	0.897	0.791	0.939	0.828	0.967	0.752	0.911	0.728	0.705	0.930	0.799
att	100	0.789	1.004	0.856	0.827	0.833	0.816	0.879	0.807	0.966	0.758	0.896	0.772	0.766	0.958	1.094
cv	5	33.6	17.1	22.1	19.4	27.2	36.1	23.5	24.3	21.1	22.4	48.4	40.3	12.2	28.7	41.5
cv	10	14.0	8.1	11.1	10.5	13.0	12.5	7.3	11.8	20.3	13.1	12.9	13.6	10.0	20.2	15.1
cv	50	17.5	21.8	17.9	14.6	21.0	18.0	11.8	14.7	16.9	11.8	16.3	16.0	8.8	13.7	15.5
cv	100	18.5	35.5	20.6	16.6	28.2	19.4	18.4	19.7	20.7	11.4	19.8	19.3	6.0	17.4	12.3

Notes: Abbreviations: avg = arithmetic mean, esd = estimated standard deviation, att = attenuation (ideal = 1), cv = coefficient of variation (relative standard deviation—expressed as a percent, ideal = 0). Each value was derived from quintuplicate measurements.

Table 3. Normalized values for emulsion formulation 7 sorted by concentration then spectrometer

material	spec	c/ppm	Fe	Ag	Al	Cr	Cu	Mg	Na	Ni	Pb	Si	Sn	Ti	B	Mo	Zn
E7Norm	0532	5	2.77	5.65	3.14	3.10	3.16	2.86	5.00	2.95	6.93	4.42	5.95	2.55	2.91	5.17	3.28
E7Norm	0620	5	2.77	5.69	3.16	2.96	3.10	2.64	4.35	2.89	4.02	4.18	4.83	2.36	3.00	3.65	3.06
E7Norm	0786	5	4.27	6.19	4.40	4.22	4.81	4.10	6.02	4.19	7.44	5.53	7.18	3.96	3.53	6.56	4.58
E7Norm	0794	5	6.03	8.31	5.17	4.66	5.82	6.30	3.33	5.08	6.80	7.21	14.27	6.23	3.71	8.28	7.96
E7Norm	0795	5	4.44	6.20	4.58	4.09	4.89	4.38	6.10	4.29	6.46	5.33	6.50	4.31	2.86	6.67	4.71
E7Norm	0532	10	5.54	11.69	6.59	6.17	6.79	5.13	9.07	6.02	10.37	7.53	7.96	5.46	6.33	9.22	6.15
E7Norm	0620	10	6.55	14.02	7.41	7.56	7.61	6.91	8.93	7.32	8.55	6.76	10.11	6.26	5.30	8.15	7.79
E7Norm	0786	10	7.50	14.02	8.49	8.17	8.99	6.78	10.64	8.12	12.47	9.46	10.87	7.42	6.98	11.28	7.85
E7Norm	0794	10	7.75	12.84	8.10	6.90	7.18	6.89	9.23	6.99	8.86	8.66	9.66	6.51	6.13	9.16	6.00
E7Norm	0795	10	7.87	14.19	6.73	7.61	9.00	7.18	9.39	8.05	13.51	7.73	11.23	7.72	5.88	13.30	8.42
E7Norm	0532	50	31.24	45.00	31.78	32.79	35.20	31.20	40.55	34.67	39.88	36.69	37.91	30.96	33.40	43.78	37.07
E7Norm	0620	50	33.23	43.98	38.98	36.56	37.98	37.08	42.25	37.25	42.57	39.07	40.17	32.67	37.32	39.94	35.85
E7Norm	0786	50	35.99	51.86	40.49	40.00	42.07	35.71	47.63	39.77	45.44	41.99	43.19	33.27	33.71	42.86	34.38
E7Norm	0794	50	43.90	58.99	49.25	44.57	51.26	45.58	50.53	46.25	54.87	39.79	50.98	40.86	39.60	50.21	43.06
E7Norm	0795	50	46.49	72.82	49.70	47.40	57.76	48.26	53.82	49.16	58.88	30.39	55.44	44.26	32.19	55.75	49.32
E7Norm	0532	100	67.38	77.35	69.02	69.33	67.58	70.10	75.05	67.06	80.79	73.47	75.25	68.54	75.29	89.61	101.96
E7Norm	0620	100	63.24	63.86	67.48	69.49	57.80	64.40	71.10	64.04	76.30	70.20	70.59	59.51	69.70	74.71	98.43
E7Norm	0786	100	78.50	102.68	88.00	84.04	83.09	81.70	91.20	81.62	97.14	89.15	91.54	77.14	77.20	95.33	112.04
E7Norm	0794	100	85.90	101.09	94.06	88.91	89.31	86.70	89.90	87.55	102.18	78.81	95.80	81.78	82.05	98.92	102.95
E7Norm	0795	100	99.40	157.01	109.33	101.63	118.97	104.90	112.05	102.99	126.73	67.17	115.00	99.02	78.70	120.59	131.68

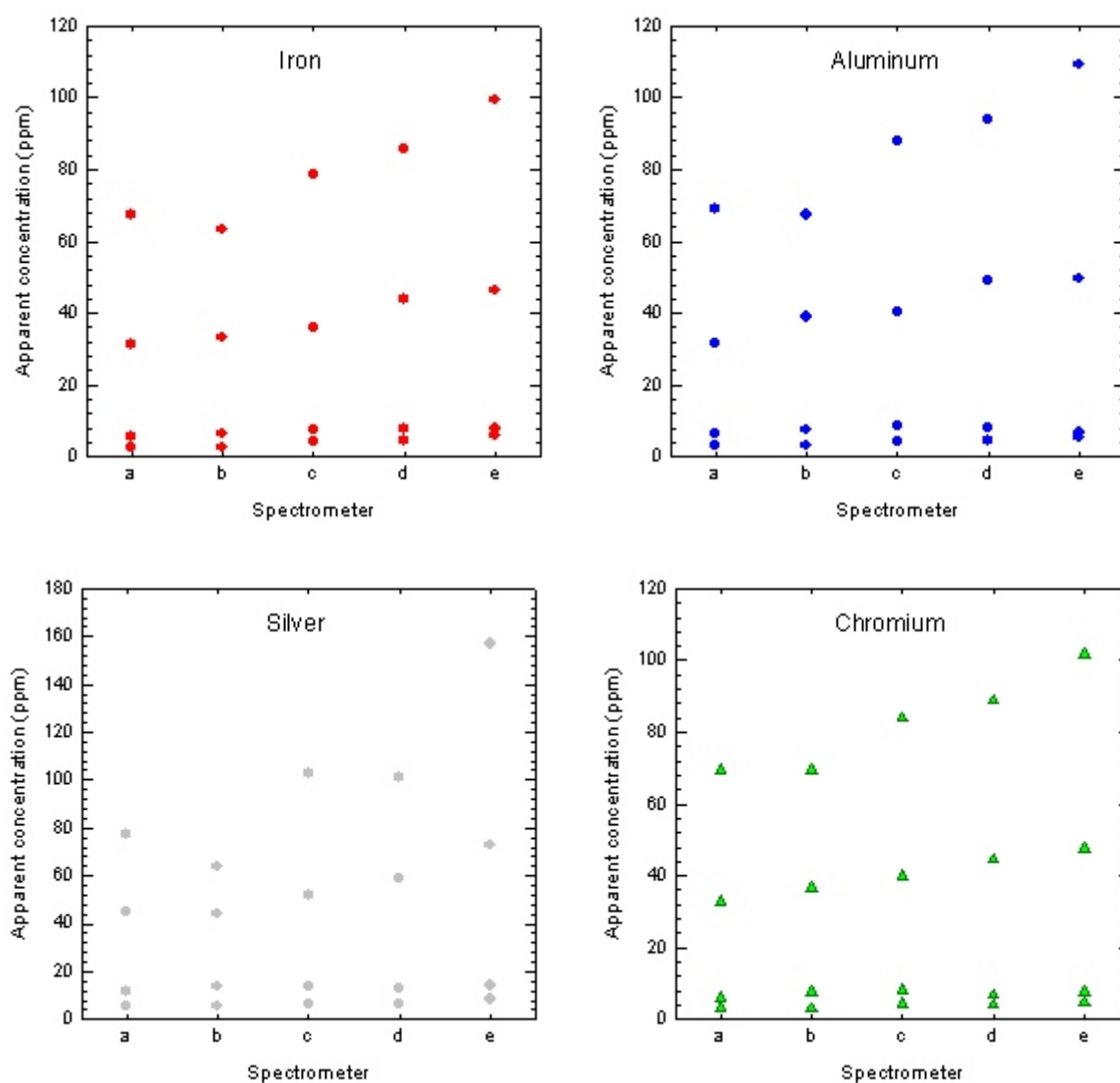


Figure 1. Trends in normalized intensity show that the effect of switching from an oleic to an emulsive matrix is associated with a systematic bias that is fairly consistent from element to element on a given spectrometer. Analyte concentrations from bottom to top: 5, 10, 50, 100 ppm. Key to spectrometers: (a) 0532, (b) 0620, (c) 0786, (d) 0795, (e) 0794.

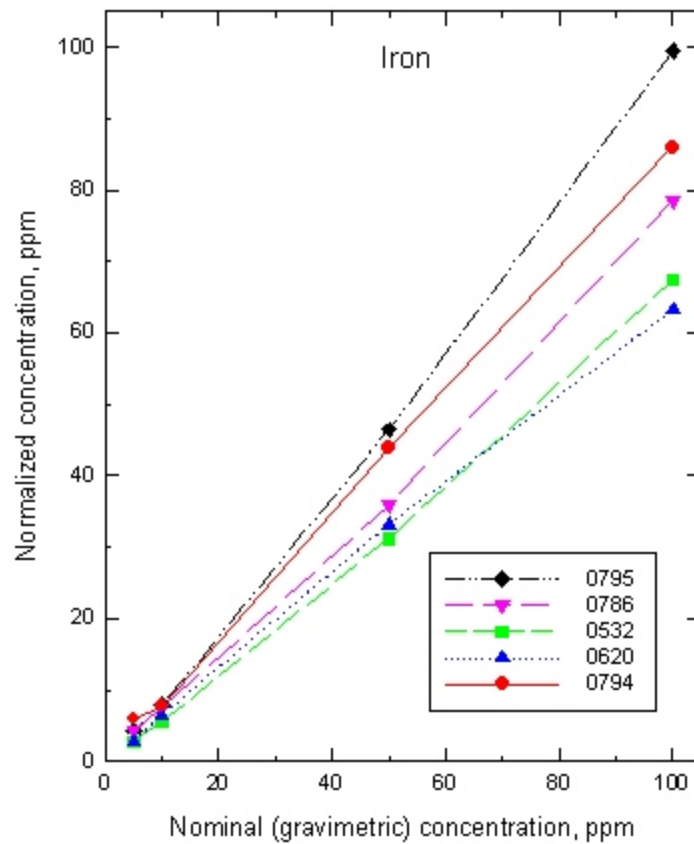


Figure 2. Normalized emulsion formulation 7 iron concentrations obtained from quintuplicate analyses on five different spectrometers show that sensitivity in the emulsive matrix varies from spectrometer to spectrometer but is essentially proportionate. The points are connected with segments (not a regression line) in a manner similar to how the spectrometer is calibrated.

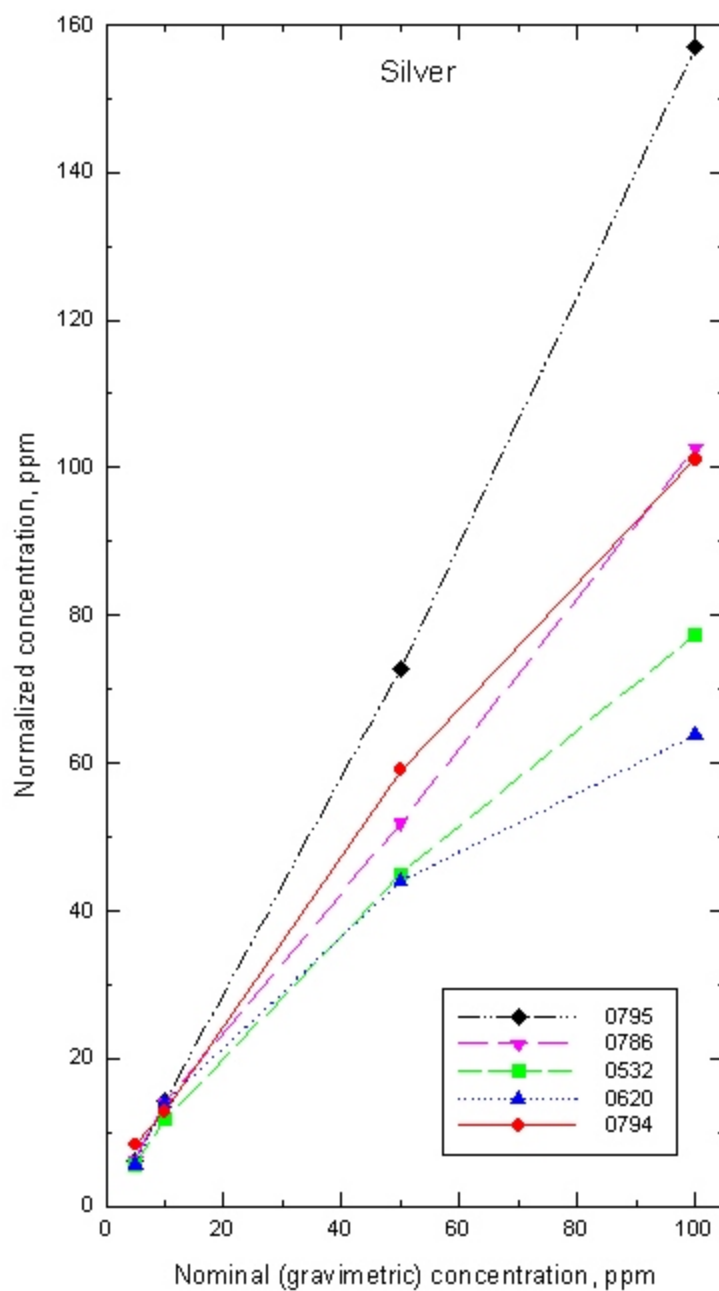


Figure 3. Normalized emulsion formulation 7 silver concentrations obtained from quintuplicate analyses on five different spectrometers show that sensitivity in the emulsive matrix varies from spectrometer to spectrometer but is essentially proportionate. The points are connected with segments (not a regression line) in a manner similar to how the spectrometer is calibrated.

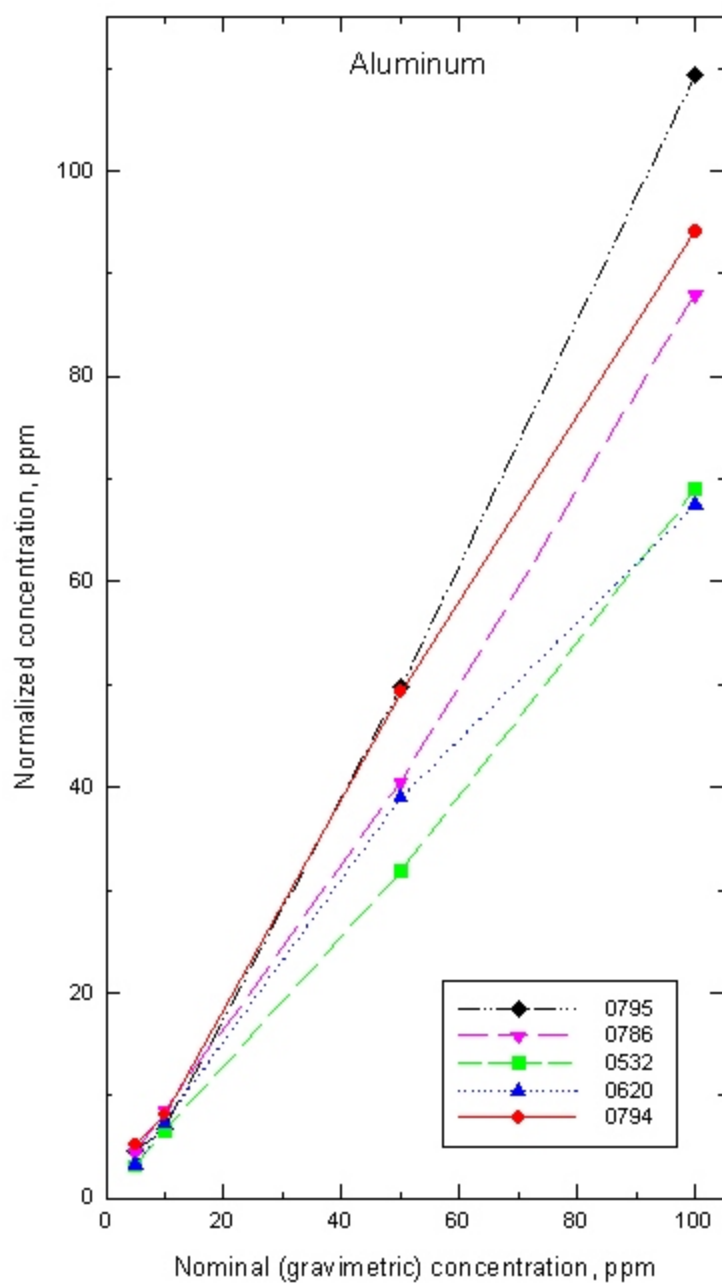


Figure 4. Normalized emulsion formulation 7 aluminum concentrations obtained from quintuplicate analyses on five different spectrometers show that sensitivity in the emulsive matrix varies from spectrometer to spectrometer but is essentially proportionate. The points are connected with segments (not a regression line) in a manner similar to how the spectrometer is calibrated.