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CHEMICAL LINEARIZATION OF CHALCOGEN RESPONSE IN A FLAME PHOTOMETRIC DETECTOR

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SUMMARY

The response of the flame photometric detector to sulfur, selenium or tellurium is normally exponential, but can be made a linear function of the amount injected by providing a high sulfur background, which increases not only the response of sulfur, but also that of selenium- and tellurium-containing compounds. Their response can be calculated approximately by a simple binomial expression. The linearity of response, within $\pm 5\%$, is demonstrated over two orders of magnitude for 1-100 ng of a sulfur analyte being determined on changing levels of sulfur background over a period of several weeks.

INTRODUCTION

The flame photometric detector (FPD) is a popular member of the family of selective detectors for gas chromatography. It responds to many elements, most notably phosphorus and sulfur¹, but also to chromium², boron³, tin⁴, selenium⁵ and others⁶⁻⁸.

One of the most frequently cited impediments to its broader use is the fact that the FPD produces an exponential response for sulfur. With a detector functioning satisfactorily, the exponent is close to 2, in accord with the species responsible for the observed chemiluminescence, S₂. As Gilbert has pointed out in an excellent review⁹, which touches on several aspects discussed in this paper, the blue bands of S₂ were known long before gas chromatography was developed and were, in fact, used to detect air pollution in Paris more than a century ago. He also discussed the spectra attributed to Se₂ and Te₂. Selenium and tellurium compounds, incidentally, yield an exponential FPD response similar to that of sulfur, at least in the upper regions of their calibration curves.

The literature on the sulfur response of the FPD is voluminous and, in addition to straightforward applications, many papers deal with the construction, operation and characteristics of various FPD types, as well as mechanistic considerations (see, for instance, refs. 10-47).

The problems of non-linear response have been dealt with in various ways, e.g., the frequent preparation of log/log calibration curves, the use of an electronic variable exponent linearization module¹⁴, the calculation of response as (peak

height)² × (width at half-height) (ref. 13), or the use of the standard additions method¹². These methods, although valuable, are likely to suffer from difficulties in the lower part of the calibration graph, where the essentially quadratic response often, and with low reproducibility, changes to a linear response.

The phenomenon of a linear lower part of the calibration curve has been used by Maitlen *et al.*⁴⁸ for insecticide residue analysis. Moss¹⁸ commented that the effect "may be used for detecting very small unwanted backgrounds... due to detector contamination or column bleed". It can be added that, say, 1 ppb (1 part per 10⁹) of a volatile sulfur compound contained in one or more of the FPD supply gases (nitrogen, oxygen, air, hydrogen), would clearly produce such an effect.

When a sulfur background is present, analyte peaks are increased by a factor $f = 1 + 2(S_B/S_A)$, where S_B is the amount of sulfur in the background and S_A the amount of sulfur in the analyte. It is obvious that improvements in detection limits can be obtained by providing a suitable sulfur background¹⁸⁻²⁰. It is also fairly obvious that a deliberately added sulfur background could be used to linearize the sulfur analyte response, but we are not aware of any studies designed to capitalize on this approach.

The extent of linearization can easily be calculated. Assume that the response R_S (peak height at constant chromatographic conditions) of a sulfur analyte A is a purely quadratic function of S_A , the amount of sulfur injected, *i.e.*, $R_S = (k_S S_A)^2$, k_S being a constant characteristic of sulfur and the particular chromatographic system.

If a background B (measured in the same units as the peak height of the analyte) is produced by continuously adding the appropriate amount of sulfur, S_B , then $B = (k_S S_B)^2$. (It is assumed that the response is not dependent on structural differences in the sulfur-containing compounds, or that the analyte and the substance responsible for the background are identical. It is also assumed that S_2 is the only emitting sulfur species, that interference from carbon, selenium, tellurium, etc., is absent, and that a possibly different method of introduction for S_A and S_B are of no major consequence when background and analyte sulfur combine in the FPD.)

The total sulfur response R (analyte response, R_S , plus background, B) can be expressed by the simple binomial

$$R = R_S + B = (k_S S_A + k_S S_B)^2 = k_S^2 S_A^2 + k_S^2 S_B^2 + 2k_S^2 S_A S_B$$

and, as $k_S^2 S_B^2 = B$, we have

$$R_S = k_S^2 S_A^2 + 2k_S^2 S_A S_B$$

Thus, the analyte response becomes the sum of two terms, one quadratic and the other linear, representing, respectively, the peak height of the analyte without the sulfur background, and the additional increment in peak height brought about by the sulfur background. Thus, it is possible to calculate the sulfur background necessary to achieve linearity of response up to a certain limit. For instance, a simple calculation shows that in order to stay within a 10% deviation from linearity, the analyte peak must not be larger than about half (44%) of the sulfur-induced background. If the

peak measures only 10% of the background, the deviation from linearity will be less than 2.5%, *i.e.*, insignificant for any practical purpose.

Similar considerations could be applied to selenium or tellurium analytes on selenium or tellurium backgrounds. However, whereas doping of the FPD with sulfur gases appears to be a reasonable proposition, a similar approach based on selenium or tellurium may fail to gain widespread acceptance. In fact, we did confirm that the response of selenium compounds increases with increasing selenium background; however, this was done only in a short experiment with appropriate precautions being taken.

Fortunately, there proved to be an easier way of enhancing and linearizing the response of selenium and tellurium. It was noticed that a sulfur background enhanced not only the sulfur but also the selenium and tellurium analyte response; similarly, a selenium background enhanced the response not only of selenium but also of sulfur analytes. (A tellurium compound was not tested in the latter experiment, nor was doping with tellurium attempted.)

There are reasons to believe that this mutual enhancement is due to the formation of interchalcogens (*e.g.*, SeS), but these arguments are beyond the scope of this paper and will be presented elsewhere. Here, we shall report on the application of sulfur doping for the linearization of the responses of sulfur, selenium and tellurium compounds in an FPD.

EXPERIMENTAL

About 2 ml of carbon disulfide were injected into a 1-A type nitrogen cylinder and the cylinder was filled with nitrogen to a pressure of 500 p.s.i. The cylinder was rolled manually for 1 h and then connected, via a pressure regulator and a fine regulating valve, to the air intake line of the FPD. The FPD was a two-channel Shimadzu model, operated with interference filters for sulfur (3940 Å, 180 Å width at half-height) and/or selenium (4839 Å, 86 Å width at half-height; a filter that was available but not necessarily the best choice for Se monitoring), or without an interference filter. The optimal gas flow-rates for the chalcogens are relatively close to each other, so that the whole experiment could be conducted with one set of conditions: hydrogen 40 ml/min, air (compressed laboratory air) 30 ml/min, nitrogen (from column) 40 ml/min and nitrogen (from carbon disulfide doping tank) as required, but generally very low. The doping tank was kept in a horizontal position with an infrared heat lamp trained on a narrow spot in its center to keep the gas circulating inside. Other chromatographic conditions were conventional and not suspected of exerting undue influence on experimental data.

Various sulfur background levels were established and test compounds containing sulfur, selenium and tellurium injected in various amounts for plotting calibration curves. To allow an assessment of selectivity against carbon compounds, a normal hydrocarbon was also tested; it gave a negative response (inverted peaks).

A practical test for sulfur linearity was conducted repeatedly over a period of a few weeks, during which the sulfur background levels changed within a limited range. Three test solutions were injected, all of which contained a sulfur "internal standard" (diphenyl sulfide) at 10 ng/ μ l and a sulfur "analyte" (*di-tert.*-butyl disulfide) at 1, 10 and 100 ng/ μ l.

RESULTS AND DISCUSSION

Fig. 1 shows the results of injecting diphenyl sulfide, diphenyl selenide and octadecane in various amounts at the different levels of sulfur doping indicated. This behavior is consistent with the consideration of sulfur response as outlined in the Introduction, and it suggests a formally similar treatment for selenium.

It may be noted that a "zero" sulfur background has been included in Fig. 1. This refers to a condition where sulfur is not deliberately added to the air supply, but where a small amount of sulfur still enters the detector inadvertently with the various gas streams necessary for its operation. This residual sulfur level can be calculated from the curvature of the calibration curve⁴⁹; in this case, it represents about 10% of the normal background.

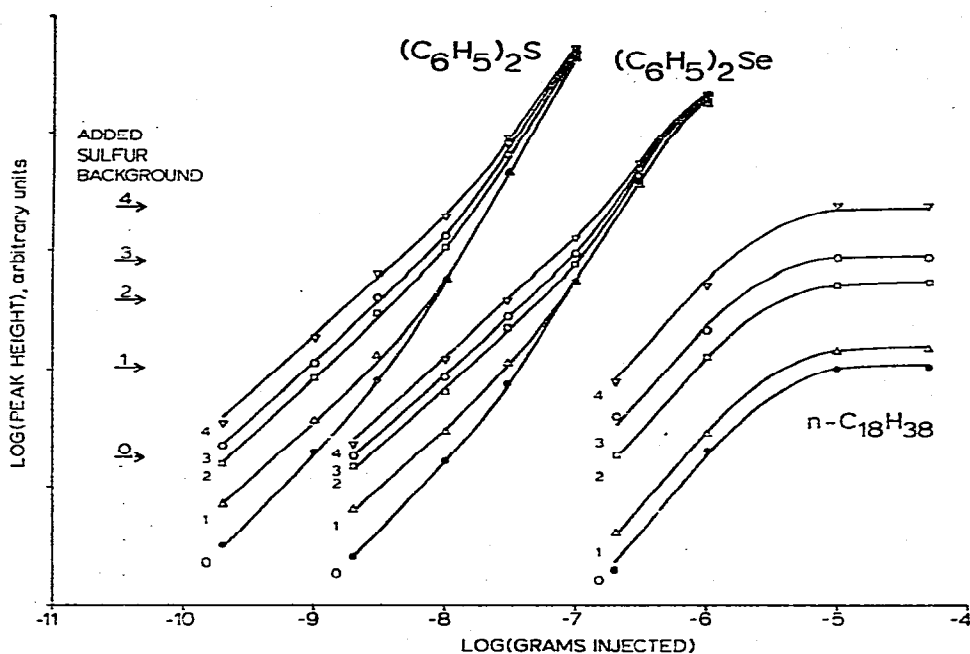


Fig. 1. Calibration graphs for diphenyl sulfide, diphenyl selenide and octadecane on different sulfur backgrounds as indicated, in a log/log plot. Octadecane peaks inverted. No interference filters used.

For analyte sulfur, as stated before,

$$R_S = k_S^2 S_A^2 + 2k_S^2 S_A S_B$$

The constant k_S can be measured in a variety of ways, two of which have been used here. Firstly, it is possible to select a clearly quadratic region of the calibration graph (S_A large, $S_B = 0$) and to calculate k_S from $R_S = k_S^2 S_A^2$. Secondly, the responses from a constant amount of analyte on different amounts of background sulfur can be measured. Fig. 2 shows such measurements in a plot of R versus \sqrt{B} for sulfur and

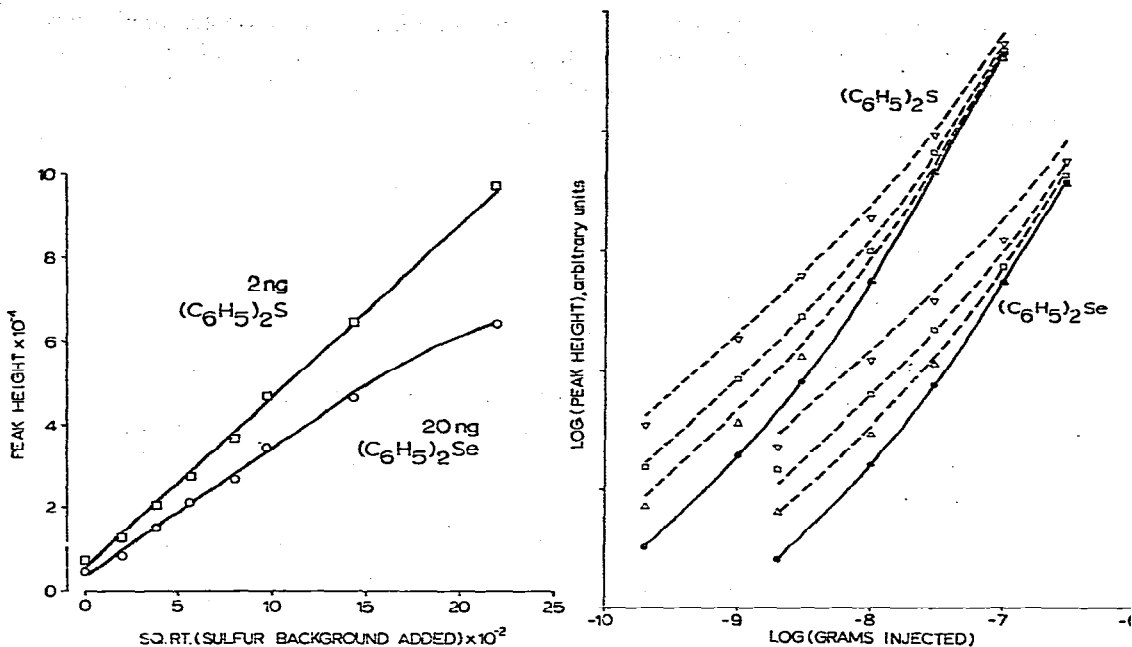


Fig. 2. Effects of sulfur background on the response of 2 ng of diphenyl sulfide and 20 ng of diphenyl selenide. No interference filters used. Responses and background in centimeters at attenuation 1 (1 cm $\approx 4 \cdot 10^{-14}$ A).

Fig. 3. Comparison of calculated and experimental responses for compounds as shown in Fig. 1. See text for method of calculation.

selenium analytes. As $\sqrt{B} = k_s S_B$, a linear relationship is obtained for the sulfur analyte:

$$R_s = k_s^2 S_A^2 + 2k_s S_A \sqrt{B}$$

and k_s can be determined from the slope, $2k_s S_A$. The values for k_s determined by the two methods were identical.

The constant k_s having been determined, calibration graphs were calculated for the sulfur analyte on the various sulfur backgrounds used. These curves are shown on the left-hand side of Fig. 3, together with the experimentally obtained data points (the "zero" line is experimental only). The pattern is well reproduced by the calculation. To view the satisfactory degree of correlation between experimental and calculated data as proof of the correctness of the approach taken would involve a circular argument; however, the procedure appears to be reasonable.

The calculation of calibration graphs becomes more difficult when the selenium response is considered on a sulfur background. The shape of these curves is similar to that of sulfur on sulfur, suggesting a similar mathematical treatment. In a purely formal analogy, a binomial expression can be written, $R = R_{Se} + B = (k_s S_B + k_{Se} S_A)^2$, where R is the total response (selenium peak height, R_{Se} , plus sulfur back-

ground, B) and k_{Se} is a constant typical of selenium, which can be determined from the quadratic portion of the graph (Se large, $S_B = 0$) from $R_{\text{Se}} = (k_{\text{Se}}Se_A)^2$. Se_A represents the amount of analyte selenium injected. Then, by analogy with the consideration of sulfur in the introductory part, we have

$$R = R_{\text{Se}} + B = (k_{\text{Se}}Se_A + k_S S_B)^2 = k_{\text{Se}}^2 Se_A^2 + 2k_{\text{Se}}k_S Se_A S_B + k_S^2 S_B^2$$

and, as $B = k_S^2 S_B^2$, we obtain

$$R_{\text{Se}} = k_{\text{Se}}^2 Se_A^2 + 2k_{\text{Se}}k_S Se_A S_B$$

i.e. the sum of a linear and a quadratic term, if the sulfur background is held constant.

Calculations on this formal basis produced calibration graphs whose patterns did correlate, although with a significant, consistent bias, with the experimental data. This bias came as no surprise; it relates to the physical meaning of the linear term $2k_S k_{\text{Se}} S_B Se_A$, the analogue of $2k_S^2 S_B S_A$ in the pure sulfur system. Here, as there, it represents the additional response generated by the sulfur background. While it is based on S_2 emission in the sulfur-sulfur system, its equivalent in the selenium-sulfur system is not established. If we assume, for instance, that the emitting species is (the unknown) SeS^* , it would be surprising if the product of the constants for S_2 and Se_2 emission, $k_S k_{\text{Se}}$, were to equal a similar expression for SeS . In other words, k_{Se} in the quadratic term and k_{Se} in the linear term would not be identical, the former relating to Se_2 , the latter to SeS emission. Expressing the constants, therefore, as k_{Se} and k'_{Se} , respectively, the formal approach is better written as

$$R_{\text{Se}} = k_{\text{Se}}^2 Se_A^2 + 2k'_{\text{Se}}k_S Se_A S_B$$

where the term $k'_{\text{Se}}k_S$ is really characteristic of the kinetic and spectral properties of the assumed interchalcogen molecule SeS or of whatever process happens to linearize the analyte response.

An experimental means of arriving at a reasonable constant for the linear term is to inject a constant amount of selenium compound on a varying sulfur background, as shown in Fig. 2. As

$$R_{\text{Se}} = k_{\text{Se}}^2 Se_A^2 + 2k'_{\text{Se}} Se_A \sqrt{B},$$

a linear plot is obtained and k'_{Se} can be calculated from the slope, $2k'_{\text{Se}} Se_A$. It is only a third (28%) smaller than k_{Se} , reflecting the similarity of the three assumed species, S_2 , Se_2 and SeS . The value for k'_{Se} thus derived can now be used (again in a circular argument) to calculate calibration graphs for a selenium analyte determined on different sulfur backgrounds:

$$R_{\text{Se}} = k_{\text{Se}}^2 Se_A^2 + 2k'_{\text{Se}} Se_A k_S S_B$$

and to compare them to experimental data points. This is shown on the right-hand side of Fig. 3. As with the pure sulfur system, the correlation is good.

Although the above lends at least a sense of self-consistency to the formal

approach taken, it must be noted that the actual situation may be more complex than suggested by the simple equations. The response, as the photomultiplier sees it in a filterless mode, results from at least two, probably from three and perhaps from even more band systems. The obvious ones are S_2 and Se_2 , the probable addition SeS , and some contributions from oxide, hydride or carbide species is always a possibility.

If a species such as SeS is formed, the S_2 bands of the background would decrease and less Se_2 (than in a non-doped system) would emit. The SeS emission would then make up for these losses and provide the additional increase in response. The possibility that increasing sulfur doping levels could change the chemical environment in a direction leading to increased emission from Se_2 should also not be discounted. A further, complicating effect is the depression of both S_2 and Se_2 bands by carbon, S_2 being the far more susceptible one⁵. As both dopant and analyte are carbon-containing compounds, the effect must be operative, but its magnitude has not been defined. Although depression of the S_2 and Se_2 bands is the major effect exerted by carbon, some emission from C_2 may also be present. Without an interference filter, the spectral characteristics of the photomultiplier tube determine the relative weights these emission bands are given in producing the "response". Clearly, the use of filters discriminates against one or the other band system that increase and decrease as an analyte peak passes through the detector.

Consider, for instance, a selenium analyte on a sulfur background. As the peak passes, the background S_2 bands decrease (this has been demonstrated experimentally) and Se_2 and the (assumed) SeS bands appear. The latter two vary in their relative magnitude during the rise and fall of the peak, reflecting the respective quadratic and linear contributions. The spectral composition of a "peak" is therefore not constant with time, as can clearly be recognized by considering the question of which wavelength it is best to select for an interference filter for "selenium" response.

Apart from spectral considerations, the main purpose of this paper was to demonstrate the analytical utility of chemical linearization. To this end, a high sulfur background was imposed on the system and the calibration graphs of sulfur and selenium compounds were obtained with sulfur and selenium interference filters (see Experimental) in place. The results are shown in Fig. 4: a linear response was obtained (the lines are drawn at precisely 45° in this log/log plot; a linear plot would also show straight lines).

This means for practical application that a single chromatographic run (including an internal standard) would suffice to produce the desired analytical result. The internal standard method is the most convenient approach to correct for shifting sulfur background and detector sensitivity levels, provided that B is high enough to keep all peaks within the linear range.

This was demonstrated by using three solutions containing 10 ng/ μ l of standard and 1, 10 and 100 ng/ μ l of analyte. These were injected repeatedly over the course of several weeks with different (but always relatively high) levels of sulfur background. Data were calculated on a linear relationship, $W_A = (R_A/R_{IS})(W_{IS}/RWR)$, where W_A and W_{IS} are the weights and R_A and R_{IS} are the responses (peak heights) of the analyte and internal standard, respectively, and RWR , the relative weight response, is a constant determined at the 10-ng level. Two typical runs are shown in Table I. The sulfur response in the 1-100-ng range was effectively linear (and selenium and tellurium would also have been linear). It may be instructive to compare the

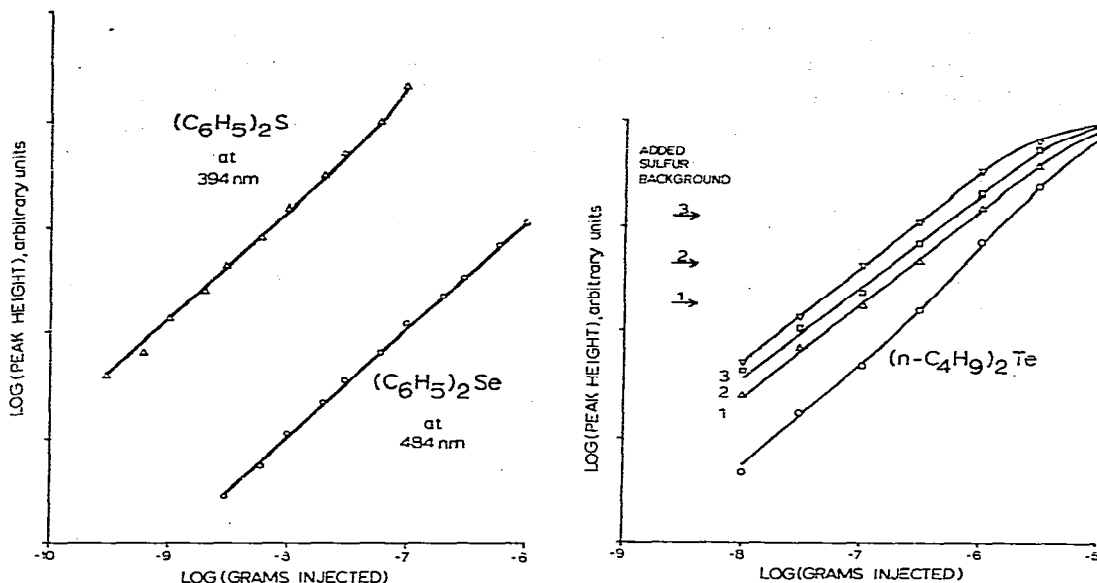


Fig. 4. Calibration graphs for diphenyl sulfide and diphenyl selenide on a large sulfur background. Interference filters as indicated.

Fig. 5. Calibration graphs for dibutyltellurium on various sulfur backgrounds as indicated, in a log/log plot. No interference filters used.

"Found" values with those expected from such a linear internal standard technique when used on a purely quadratic system. Correlating at the 10-ng level, 0.1 and 1000 ng would have been "found" for the 1- and 100-ng levels, respectively. This fact considered, the accuracy obtained is remarkably good.

A few caveats should be noted in this context. The sulfur background has to be large enough (about double the size of the largest peak for less than a 10% deviation from the true value) to ensure linearity; however, care has to be taken not to reach a concentration range where saturation of the system begins to occur.

The light level of the FPD is high under these circumstances and it may be necessary to employ filters or masks to prevent damage to the photomultiplier tubes and to keep within read-out capabilities. Use of masks and/or filters decreases the sensitivity (and may increase the selectivity). The effect was not very important in our system (*i.e.*, it did not exceed a factor of 3).

TABLE I

TYPICAL LINEAR CALCULATIONS OF ANALYTE CONTENT BY THE INTERNAL STANDARD TECHNIQUE

Internal standard* (ng)	Analyte** (ng)	Found (1) (ng)	Found (2) (ng)
10.0	1.00	0.94	1.05
10.0	10.0	9.8	10.2
10.0	100	102	100

* Internal standard: diphenyl sulfide.

** Analyte: di-*tert.*-butyl disulfide.

Operating on a high sulfur background also brings with it some loss in signal-to-noise ratios, which is easy to understand. Noise increases, to a first approximation, with total light emitted. The increase in background is a quadratic function of sulfur doping and the increase in analyte response is a linear function. Hence the signal-to-noise ratio for an analyte peak will increase with increasing background to a maximum (in our system roughly four times the value obtained without a deliberately added sulfur background), but then decline. Consequently, the minimum detectable limits in a high-background system designed for a maximum linear range can be, and were in our case, higher than those obtained under non-doped conditions. The effect, however, was minor within the range of sulfur backgrounds used.

This study was, of course, designed to demonstrate a reasonable linear range (two decades) beyond that normally obtained; this may be excessive for practical samples, the chalcogen concentrations of which may be close to the minimum detectable limits and for which, therefore, a lower sulfur background would result in better analytical data. This may be particularly appropriate to selenium or tellurium, whose (very approximate) sensitivities are only 0.1 and 0.01 times that of sulfur, respectively.

The study of the standard compound dibutyltellurium was marred by the need to prepare freshly diluted solutions prior to injection. Despite the greater variations in the data, however, it is clear that tellurium behaves similarly to selenium (and sulfur) in the increase and linearization of its response with increasing sulfur background levels. In fact, linearization appears to be achieved more easily than with the other two chalcogens, as shown in Fig. 5. Whether this is due to a larger constant k'_{Tc} characteristic of the formation of, and emission by, an (assumed) interchalcogen TeS , or, perhaps, a contribution by TeO or other possible emitters, has not been further investigated.

To conclude, it now appears feasible in practical analysis to linearize the chalcogen response by chemical means in an FPD and to predict, at least to some extent, the levels of sulfur background that are necessary to achieve a desired linear range.

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