

## ESTIMATION OF LIMITS OF DETECTION FOR THE FLAME EMISSION GAS CHROMATOGRAPHIC DETECTOR

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WINEFORDNER AND VICKERS<sup>1</sup> have used signal-to-noise ratio theory to derive an expression for calculating the limiting detectable atomic concentration in atomic emission flame spectrometry. The evaluation of such an expression requires a detailed knowledge of instrumental, spectral, and flame compositional parameters. The usefulness of such an expression, and its evaluation is threefold: estimation of limits of detection; estimation of optimum conditions of measurement; and estimation of the influence of variation in parameters on the limit of detection. Such estimates aid the analyst in obtaining the lowest limits of detection in atomic emission flame spectrometry.

## THEORETICAL CONSIDERATIONS

The system under consideration consists of a flame source (turbulent flame produced by a total-consumption aspirator-burner or a laminar flame produced by a chamber-type aspirator-burner), suitable entrance optics (a lens, mirror, combination of two, or none), a monochromator (prism or grating) or interference filter, a photodetector, electrometer, and readout (recorder, meter, etc.). It will be assumed that the brightest part of the outer cone of the flame is always selected for viewing. It is also assumed that the width,  $W$ , and height,  $H$ , of the entrance and exit slits of the monochromator (if used) are identical (this is generally the case for most commercial monochromators—anyway, little gain in signal-to-noise ratio and no gain in resolution results if the slits are unequal). Under these conditions, the major sources of noise at the limit of detection are the phototube shot noise and the flame background flicker noise. Generally with any good instrumental system, electrometer noise<sup>2</sup> can be made negligible; and, when using multiplier phototubes, Johnson noise is also negligible. Flicker noise due to flicker in the measured atomic line is necessarily negligible at the limit of detection. It is, of course, also assumed that the gas chromatographic peak of interest is completely resolved.

The limit of detection is defined<sup>3</sup> as that atomic concentration,  $N_m$ , in total number of atoms of the species in concern in all states per  $\text{cm}^3$  of flame gas, resulting in a signal-to-noise ratio of  $t\sqrt{2}/\sqrt{\bar{p}}$ , where  $t$  is the student "t" which can be found in statistics tables for a given confidence level and a given number of degrees of freedom ( $2\bar{p} - 2$ ), and  $\bar{p}$  is the number of combined sample plus background observations. Using this limit of detection definition and the expression given by WINEFORDNER AND VICKERS<sup>1</sup> for atomic emission flame spectrometry, an expression for the limiting

detectable atomic concentration,  $N_m$ , for the flame emission gas chromatographic detector<sup>4-7</sup> when measuring *atomic emission* can be obtained, *i.e.*,

$$N_m = \frac{2.7 \cdot 10^{34} I_B(T) e^{E_u/kT} \sqrt{2eBM\Delta f[i_d + \gamma T_f I_B WH\Omega s] + \Delta f[\gamma T_f \xi I_B WH\Omega s]^2}}{\sqrt{\bar{p} n \kappa g_u \nu_0 A_t \gamma T_f WH\Omega}}$$

where all terms are defined in the Appendix. The evaluation of all terms is also discussed in the Appendix. In the above expression, it has been assumed that the measured spectral line is single, sharp, and isolated. If a multiplet is being measured, then  $\exp(E_u/kT)/\kappa g_u \nu_0 A_t \gamma T_f$  must be replaced by:

$$\sum_i \frac{\exp(E_{u_i}/kT)}{\kappa_i g_{u_i} \nu_{0_i} A_{t_i} \gamma_i T_{f_i}}$$

where the summation is over all spectral lines being measured. Because all spectral components will not be passed centrally through the exit slit,  $\kappa_i$  will be less than unity for each spectral line. As long as the measurements are made between about 2800–5400 Å, and as long as the spectral band width is not large (10 mμ or less), then the photoanodic sensitivity of the photodetector,  $\gamma_i$ , will be essentially the same for all components. Also the peak frequencies,  $\nu_{0_i}$ , and the energies of the upper levels,  $E_{u_i}$ , of each spectral component (assuming lower level of the transitions is the ground state or a state close to the ground state) are essentially the same and can be replaced with an average peak frequency and an average energy although it is no more difficult to substitute the exact values of  $\nu_{0_i}$  and  $E_{u_i}$ . The transmission factor of the optical system,  $T_f$ , will be slightly different for each spectral component but under most experimental conditions (see above) will be approximately the same for all spectral lines. Therefore, if a multiplet is being measured and if a good quality optical instrument, *e.g.*, a Beckman DU prism monochromator, is used, then only  $\kappa_i$  and  $A_{t_i}$  will vary appreciably for each measured spectral component.

Most analysts are not interested in limiting detectable atomic concentrations, but rather in limiting detectable sample sizes introduced into the gas chromatographic system. By means of an approach similar to that used by WINEFORDNER AND VICKERS<sup>1</sup> to convert atomic concentrations in the flame gases to sample concentration aspirated into the flame, it is possible to derive an expression relating  $N_m$  to the minimum detectable sample weight,  $w_m$ , in grams, introduced into the gas chromatographic column, *i.e.*, a sample weight of  $w_m$  results in a peak which is discernible from the noise with the desired degree of confidence. The derived expression is:

$$w_m = \frac{N_m M_w Q e_f t_c}{\alpha \beta N_0}$$

where  $M_w$  is the molecular weight of the species introduced into the gas chromatographic column, in grams/mole;  $Q$  is the flow rate<sup>1</sup> of unburnt flame gases in cm<sup>3</sup>/sec.;  $e_f$  is the flame gas expansion factor<sup>1</sup> and is given approximately by the ratio  $n_T T/T_R n_R$ , where  $n_T$  and  $n_R$  are the number of moles of flame gas combustion products at the flame temperature,  $T$ , and room temperature,  $T_R$ , respectively;  $\alpha$  is a factor needed to

convert moles of molecular sample to moles of measured atoms in all forms, *e.g.*, for chromium hexafluoroacetylacetonate, it is unity, since there is one chromium atom per molecule;  $\beta$  is the atomization efficiency factor<sup>8</sup> to account for compound formation and ionization of the species of interest in the flame gases;  $N_0$  is Avogadro's number, *i.e.*,  $6.02 \cdot 10^{23}$  particles/mole; and  $t_c$  is the residence time of the sample in the detector (see Appendix). The evaluation of these parameters is discussed in the Appendix.

## DISCUSSION

By means of the expression for  $N_m$ , it is possible to estimate limiting detectable atomic concentrations for any element emitting line spectral in the ultraviolet-visible region; and therefore, to compare measurement systems, flame types, and spectral lines for such elements. In this way, it is possible to optimize the instrumental system to measure the smallest detectable atomic concentration. By means of the expression for  $w_m$  and the result of the  $N_m$  calculation, it is possible to predict the smallest amount of sample detectable by using the flame emission gas chromatographic detector. Such calculations should enable the analyst to determine the feasibility of using the flame emission detector as well as predicting the optimum experimental conditions for measurement. Finally, such a theoretical approach should aid the analyst in explaining the causes of interferences which result in a deviation from the theoretical relationships given here.

Because of a lack of information concerning experimental parameters in the papers by JUVET and co-workers<sup>4-6</sup>, it is not possible to compare with any accuracy experimental and calculated limits of detection. However, even if JUVET and co-workers<sup>4-6</sup> had given measured values of such parameters as  $t_c$ ,  $W$ ,  $T$ ,  $\gamma$ ,  $BM$ , etc., it would still be difficult to compare calculated limiting detectable sample sizes,  $w_m$ , with experimental values of  $w_m$  because of the lack of accurate values of the efficiency of atomization,  $\beta$ . This points out the importance of experimental measurement of  $\beta$  values for a variety of atoms in a number of analytical flames. DE GALAN AND WINEFORDNER<sup>8</sup> have measured  $\beta$  values for over 20 elements in an  $C_2H_2$ /air flame.  $\beta$  values of the same elements in other flames could be measured by similar techniques. Because of a lack of reliable spectroscopic data, it is impossible to calculate accurate  $\beta$  values from thermodynamic equilibrium constants of processes occurring in the flame gases, and so  $\beta$  values should be experimentally measured for the atom and flame type in concern.

For instructive purposes, however, a calculation of  $N_m$  and  $w_m$  will be performed for a sample of chromium hexafluoroacetylacetonate such as measured by JUVET AND DURBIN<sup>4,5</sup>. For this case, it will be assumed that an experimental set-up similar to the one used by JUVET AND DURBIN<sup>4,5</sup> is used, *i.e.*, the output of the gas chromatographic column is introduced into a medium-bore total consumption aspirator-burner with a  $H_2/O_2$  flame, and the emission of the Cr-triplet (4254, 4275, 4290 Å) is measured by means of a Beckman DU monochromator with 1P28 multiplier phototube and a d.c. amplifier readout with a frequency response bandwidth,  $\Delta f$ , of  $1 \text{ sec}^{-1}$ . The spectral parameters of  $g_u A_t$  and  $E_u$  are taken as  $2.0 \cdot 10^8$ ,  $1.5 \cdot 10^8$ ,  $0.95 \cdot 10^8$  and 2.91, 2.90, 2.89, respectively, for the 4254, 4275 and 4290 Å lines. The partition function  $B(T)$  for the Cr atom in a flame of 2700 °K is 7.43. The frequencies

of the 4254, 4275, and 4290 Å lines are  $7.05 \cdot 10^{14}$ ,  $7.02 \cdot 10^{14}$ , and  $6.99 \cdot 10^{14}$ ,  $\text{sec}^{-1}$ , respectively. The instrumental factors of  $W_0$  (calculated from equation in text),  $H$ ,  $\Omega$ ,  $s$  ( $s = R_d W_0$ ),  $T_f$ ,  $i_d$ ,  $BM$ , and  $\gamma$  (assuming —1000 V applied to photocathode of phototube) are 0.016 cm, 1 cm, 0.01, 2.07  $\text{m}\mu$ , 0.5,  $3 \cdot 10^{-10}$  A,  $3 \cdot 10^6$ , and  $6 \cdot 10^4$  A/W. The values of  $\kappa$  for the three lines (assuming the monochromator is set at  $\lambda = 427.5$   $\text{m}\mu$ ) are 0.10, 1.00, and 0.28, respectively, if the spectral bandwidth is 2.07  $\text{m}\mu$ . The flame parameters of  $T$ ,  $L$ ,  $Q$ ,  $e_f$ , ( $e_f = n_T T / n_R T_R$ ),  $\xi$ ,  $I_B$ , and  $\beta$  are taken as 2700 °K, 0.5 cm, 50  $\text{cm}^3 \cdot \text{sec}^{-1}$ ,  $e_f = 1.2 \cdot 2700 / 298 = 10.8$ , 0.005  $\text{sec}^{1/2}$ ,  $10^{-8}$  W  $\text{cm}^{-2}$  ster. $^{-1}$   $\text{m}\mu^{-1}$  (estimated from data given by GILBERT<sup>10</sup>) and 0.06 estimated from DE GALAN AND WINEFORDNER<sup>8</sup>, respectively. Other parameters needed for the calculation are given the following values:  $t\sqrt{2}/\sqrt{p} = 2.0$  (for  $p = 6$  at 99.5 % confidence level);  $t_e = 1$  sec (estimated from our experience);  $\alpha = 1$  (for chromium hexafluoroacetylacetonate); and  $M_w = 676$  g mole $^{-1}$ .

Using the above values of parameters which are characteristic of a standard gas chromatographic and spectrometric system, such as used by JUVET AND DURBIN<sup>4, 5</sup>,  $N_m$  and  $w_m$  are found to be approximately  $1.3 \cdot 10^8$  atoms  $\text{cm}^{-3}$ , and  $1.2 \cdot 10^{-9}$  g. JUVET AND DURBIN<sup>5</sup> reported a value of  $w_m$  of  $6.8 \cdot 10^{-8}$  g for the measurement of the Cr-triplet obtained by introducing chromium hexafluoroacetylacetonate into their gas chromatographic-spectrometric system. Part of the discrepancy is certainly due to the use of a non-optimum monochromator slit width by JUVET AND DURBIN<sup>4</sup> although the largest discrepancy is very likely in our choice of  $\beta$  for our calculation of  $w_m$  from  $N_m$ .

Perhaps the greatest use of the equations for  $N_m$  and  $w_m$  lies in predictions of which factors and to what extent these factors influence  $N_m$  and  $w_m$ . For example,  $N_m$  (and therefore,  $w_m$ ) is quite sensitive to the monochromator slit width.

By differentiating the  $N_m$  expression with respect to monochromator slit width,  $W$ , and minimizing, the optimum monochromator slit width,  $W_0$ , in cm, can be found. This was done by WINEFORDNER AND VICKERS<sup>1</sup> who give the following expression for  $W_0$ :

$$W_0 = \sqrt[4]{\frac{2eBM}{[\gamma T_f \xi I_B \Omega R_d]^2}}$$

where all terms and their evaluation are discussed in the Appendix. It is also evident from the equation for  $N_m$  that the smaller the frequency response bandwidth,  $\Delta f$ , the smaller  $N_m$  (and  $w_m$ ). Of course, the value of  $\Delta f$  must be considerably larger than  $t_e^{-1}$  in order to record accurately the peak shape. In addition,  $\Delta f$  must be larger than about 0.1  $\text{sec}^{-1}$  to avoid problems associated with drift in the flame gas flow rates. An increase in flame temperature,  $T$ , results in a decrease in the Boltzmann factor in the equation for  $N_m$  but also an increase in  $I_B$ . As long as  $\exp(E_u/kT)$  decreases faster than  $I_B$  increases, a decrease in  $N_m$  will result. Of course, flame temperatures and composition influences  $\beta$ , and so even though  $N_m$  may decrease, it is possible that  $w_m$  may not change or may even increase as flame temperature increases. Therefore,  $w_m$  is a complex function of  $T$ . However, an optimum flame temperature giving a minimum  $w_m$  should exist for most atomic species. The importance of the choice of flame type is certainly evident from the above discussion concerning the influence of  $T$  on  $\beta$ ,  $I_B$ , and  $\exp(E_u/kT)$ . However, an additional flame parameter, namely, the

flame flicker factor,  $\xi$ , should also be considered. For example, a low background flame, such as a  $H_2$ /air flame, which also has a low flame flicker noise could result in lower values of  $N_m$  than a high background but high temperature flame, such as  $C_2H_2$ /air. Lower values of  $N_m$  (and  $w_m$ ) will also result if the thermionic dark current,  $i_d$ , is reduced by cooling the photocathode of the multiplier phototube. Most other parameters in the  $N_m$  equation for a given atom-line and a given instrumental system are fixed or have little or no effect on  $N_m$ , e.g.,  $H$ ,  $\Omega$ ,  $R_d$ ,  $T_f$ ,  $BM$ ,  $\gamma$ ,  $g_u$ ,  $v_0$ , and  $A_t$ . The entrance optics factor,  $n$ , can also be varied, but the effect on  $N_m$  is relatively complex, since not only does the numerator of  $N_m$  increase but also the measured flame background intensity,  $I_B$  increases approximately linearly with  $n$ .

The expression for  $N_m$  could also be used to approximate limiting detectable concentrations of molecules which emit in the flame gases, e.g., AlO, CH, CN, etc., if it is assumed that the molecular band is approximately Gaussian and that the spectral bandwidth,  $s$ , of the monochromator is narrow compared to the Gaussian half-width,  $\Delta\lambda$ , in  $m\mu$ , of the molecular band. In this case, the expression for  $N_m$  needs only to be multiplied by  $s/\Delta\lambda$  assuming the monochromator is set at the band peak. Of course, if the monochromator is not set at the band peak or if vibrational-rotational fine structure is present, then deviations occur unless the fine structure and emission band profile are accounted for in detail<sup>13</sup>. However, it should still be possible to approximate limits of detection for species introduced into gas chromatographic columns which result in molecular species in the flame gases.

If an interference filter rather than a monochromator is used, the same expression for  $N_m$  can be used. However in this case, the spectral bandwidth,  $s$ , is the half-intensity bandwidth of the filter and  $W$  and  $H$  in the  $N_m$  equation correspond to either the source width and height or detector width and height depending upon which is smaller. The solid angle,  $\Omega$ , is determined by the optical setup; if no baffles are used, then it should be determined by the size of the detector and the distance from the flame source to the detector.

## APPENDIX

### *Definition, units, and methods of measurement of parameters*

- $A_c$  = Effective aperture of monochromator,  $cm^2$ . Measure or obtain from manufacturer's literature.
- $A_t$  = Transition probability of spontaneous emission,  $sec^{-1}$ . Obtain from literature<sup>9</sup>.
- $B$  = Multiplier phototube factor, no units.  $B \cong G^x + G^{x-1} + \dots + G + 1$ . Measure or estimate from manufacturer's literature.
- $B(T)$  = Electronic partition function of atom, no units. Table of these values for about 50 elements between 1500 and 7000°K available from principal author by request.
- $E_u$  = Energy of state,  $u$ , eV. Obtain from literature<sup>9</sup>.
- $e$  = Electronic charge,  $1.6 \cdot 10^{-19}$  coulombs.
- $e_f$  = Flame gas expansion factor, no units. Calculate from ratio  $n_T T / n_R T_R$ .
- $\Delta f$  = Frequency response bandwidth of electrometer-readout system,  $sec^{-1}$ . Can be estimated from characteristics of electrometer output and recorder.
- $F$  = Flow rate of carrier gas in gas chromatograph,  $cm^3 \cdot sec^{-1}$ . Measure by soap bubble flow meter or similar device.

- $F_c$  = Focal length of collimator of monochromator, cm. Measure or obtain from manufacturer's literature.
- $g_u$  = Statistical weight of upper state involved in transition, no units. Obtain from literature<sup>9</sup>. Actually  $g_u A_i$  is obtained from literature<sup>9</sup>.
- $G$  = Gain per dynode of multiplier phototube, no units. Measure or estimate from manufacturer's literature.
- $H$  = Monochromator slit height, cm. Measure or obtain from manufacturer's literature.
- $h$  = Planck's constant,  $6.62 \cdot 10^{-27}$  erg. sec.
- $i_d$  = Phototube thermionic dark current, amperes. Measure by means of electrometer or estimate from manufacturer's literature.
- $I_B$  = Flame background intensity, watts  $\text{cm}^{-2}$  ster.<sup>-1</sup> $\text{m}\mu^{-1}$ . Measure or estimate from literature<sup>10</sup>.
- $k$  = Boltzmann constant,  $8.62 \cdot 10^{-5}$  eV  $^\circ\text{K}^{-1}$ .
- $L$  = Flame diameter, cm. Measure effective diameter of luminous portion of flame gases by photograph or by imaging flame on a flat surface.
- $M$  = Multiplier phototube amplification factor, no units.  $M = G^x$ . Measure or estimate from manufacturer's literature.
- $M_w$  = Molecular weight of species introduced into the gas chromatographic column, atomic mass units.
- $n_R$  = Number of moles of flame gas products (reactants) at room temperature. Estimate from tables of ZAER<sup>11</sup>.
- $n_T$  = Number of moles of flame gas products at the flame temperature. Estimate from tables of ZAER<sup>11</sup>.
- $N_m$  = Limiting detectable atomic concentration of species in concern, atoms  $\text{cm}^{-3}$ .
- $N_0$  = Avogadro's number,  $6.02 \cdot 10^{23}$  particles mole<sup>-1</sup>.
- $p$  = Number of combined sample-background readings taken at the limit of detection, no units.
- $Q$  = Flow rate of unburnt gases into flame,  $\text{cm}^3 \cdot \text{sec}^{-1}$ . Measure by monitoring flow of flame gases.
- $R_d$  = Reciprocal linear dispersion of monochromator,  $\text{m}\mu \text{ cm}^{-1}$ . Measure by use of a discharge tube spectrum or obtain from manufacturer's literature.
- $s$  = Spectral bandwidth of monochromator,  $\text{m}\mu$ .  $s \cong R_d W$  for line and continuous sources.
- $t$  = Student "t". Find in statistics tables.
- $t_c$  = Residence time of sample in cell, sec. Assuming a triangular distribution of sample in gas chromatographic column,  $t_c = V/F$ , sec, *i.e.*,  $t_c$  is assumed to be the half-width in seconds of the gas chromatographic peak. Since the peak will undoubtedly be more Gaussian than triangular the half-width of the Gaussian peak can be converted to half-width (in time) of the triangular peak by multiplying the measured half-width in seconds by  $\sqrt{\pi}/2\sqrt{\ln 2}$  or 0.94. A basic assumption inherent here is that the response time of the readout does not limit the shape of the gas chromatographic peak or if it does affect the peak shape it is accounted for.
- $T$  = Flame temperature,  $^\circ\text{K}$ . Measure or estimate by method described by WINEFORDNER, MANSFIELD AND VICKERS<sup>12</sup>.

- $T_f$  = Transmittance of optical system, no units. Measure or estimate from manufacturer's literature.  
 $T_R$  = Room temperature, °K.  
 $V$  = Volume of detector cell, cm<sup>3</sup>.  
 $W$  = Monochromator slit width, cm.  
 $w_m$  = Limiting detectable sample size, g.  
 $W_0$  = Optimum monochromator slit width, cm. Calculate as described in text.  
 $x$  = Number of dynodes in multiplier phototube, no units.  
 $\alpha$  = Factor to account for moles of measured species per mole of species introduced into the gas chromatograph, no units.  
 $\beta$  = Efficiency of atomization, fraction of element in concern in flame gases in form of atoms to element in concern in all forms, *i.e.*, as compounds formed with flame gas products and as ions as well as atoms in all electronic states. DE GALAN AND WINEFORDNER<sup>8</sup> describe the measurement of  $\beta$  factor for a number of atoms in an C<sub>2</sub>H<sub>2</sub>/air flame.  
 $\gamma$  = Photoanodic sensitivity of multiplier phototube, amps·watt<sup>-1</sup>. Measure or estimate from manufacturer's literature.  
 = Monochromator slit function parameter, no units. assuming a triangular slit function.<sup>13</sup>

$$\kappa = 1 - \frac{|\lambda - \lambda_0|}{s}$$

- $\lambda$  = Wavelength setting of monochromator, m $\mu$ .  
 $\lambda_0$  = Wavelength of line center, m $\mu$ .  
 $\nu_0$  = Frequency of line center, sec<sup>-1</sup>.  
 $\xi$  = Ratio of root-mean-square fluctuation in the background intensity to the background intensity, sec<sup>1/2</sup>. Measure as described by VICKERS<sup>14</sup> or estimate from literature.  
 $\Omega$  = Solid angle of radiation collected by monochromator assuming effective aperture is filled with radiation, ster.  $\Omega = A_e/F_e^2$ .

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#### SUMMARY

The limit of detection theory proposed by WINEFORDNER AND VICKERS for atomic emission flame spectrometry is applicable to estimation of limits of detection when using the flame emission gas chromatographic detector. Expressions are given for the limiting detectable concentration of the species in concern in the flame gases and for the limiting detectable sample size introduced into the gas chromatographic system when measuring line radiation from radiational deactivation of excited atoms. By means of several assumptions, these same expressions, modified slightly, can be used if the emitting species is a molecule. The expressions given can be

used to estimate limits of detection and to optimize the experimental system with respect to gas chromatographic, flame compositional, spectral, and instrumental parameters. The variation of these parameters on the limiting detectable atomic concentration in the flame gases and on the limiting detectable sample size introduced into the gas chromatographic system is discussed.

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