

OPTIONS IN GAS CHROMATOGRAPHIC TECHNIQUES FOR MEASUREMENT OF H₂S IN FUEL GAS

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ABSTRACT

To reduce the negative environmental effects of acid rain, federal environmental regulations require limits on the emission of SO₂ from combustion processes. In many hydrocarbon processing plants, the choices for measuring and controlling SO₂ include the indirect method of measuring H₂S in the fuel gas used for furnaces and other process combustion units. The federal regulations specify a limit on the quantity of H₂S that is permitted in such fuel gases and one common method for measuring the H₂S concentration in fuel gas is with process gas chromatography. But two markedly different chromatographic methods also exist which involve using thermal conductivity detection in one case and flame photometric detection in the other. This paper looks at the two techniques and provides comparisons of their relative advantages and disadvantages. Additionally, the potential of the two techniques for modification is considered in light of current discussions about possible further changes in the federal regulations.

INTRODUCTION

Concerns about environmental damage caused by industry began to arise in the US in the latter part of the 20th century. One major issue that caught the attention of the public and regulators in the 1960's and '70s was deforestation resulting from significant damage to trees over large areas. The damage, including discoloration, susceptibility to disease and death was found to be caused by exposure to sulfuric acid: H₂SO₄ in aqueous solution. The acid, in turn, was found to be

created when large quantities of SO₂ vapor emitting from combustion processes combined with water in the atmosphere in the presence of light and then precipitated in rain. The phenomenon is referred to as acid rain and reduction of acid rain became a very early priority in United States Clean Air Act legislation intended to protect the environment.

To reduce acid rain, industries operating combustion processes are required to reduce the release of SO₂ into the atmosphere and subsequently to document quantities of SO₂ being released by continuous measurement. Various methods for direct measurement of the SO₂ being released from combustion processes may be considered. However, direct measurements in stack effluents are often problematic because of severe ambient environments and the difficult maintenance conditions. Such techniques were generally not available in reliable or cost effective hardware. Furthermore, in situ cross-stack techniques and extractive techniques involve assumptions that the point of measurement is representative of the whole of the emission. In large combustion processes, such as furnaces used for cracking in olefins manufacturing, these assumptions are difficult to validate.

However, the U.S. Environmental Protection Agency (EPA) has approved the measurement of sulfur in the fuels that will be burned and permits determination of the SO₂ that will be released to the atmosphere based on the quantity of sulfur in the fuels⁽¹⁾. In principle, this kind of practice would require the measurement of total sulfur in all of its elemental and chemical forms in the fuel. However, the EPA has further approved the generalization that in vapor hydrocarbon fuels, a measurement of the single sulfur compound, hydrogen sulfide (H₂S) would be sufficient for a good approximation of the total SO₂ that would result. The premise is that H₂S in particular constitutes an overwhelmingly major percentage of the sulfur that might be present in hydrocarbon fuel gas.

This solution proved particularly valuable to the hydrocarbon processing industries that burn various waste and plant gases to create heat for cracking furnaces because the fuel gases being burned are well contained in pipelines and are easily sampled and measured. Furthermore, the measurement itself can be performed with well known, simple and maintainable methods.

These principles and methods along with target limits; test, validation and calibration methods; data reporting and logging requirements; and, operational standards were incorporated into the Code of Federal Regulations (CFR) in the 1980's and went into enforcement in the early 1990's. The relevant portions⁽¹⁾ were "40 CFR 60 Subpart J". Subsequent amendments have been made and these are referred to as "40CFR 60 Subpart Ja", which was promulgated in June 2008 but affected construction as early as May 2007.

Today, process solutions or potential solutions for measuring H₂S in fuel gas include gas chromatography, extractive optical methods such as tunable diode lasers⁽⁶⁾ and others. However, chromatography in particular is the technique which has been in use the longest and is the most widely characterized and understood. Therefore, this paper deals specifically with a comparison of particular chromatographic techniques for measuring H₂S in fuel gas. Note, further, that a complete Continuous Emissions Monitoring System (CEMS) for this purpose must comply with several requirements including data logging, reporting and validation requirements. This paper

is concerned only about the issues directly affecting chromatographic measurement and the use of chromatographs for this purpose.

APPLICATIONS AND MEASUREMENT REQUIREMENTS

In hydrocarbon processing plants, such as olefins manufacturing facilities, the most common requirement for measurement of H₂S in fuel gas is on the fuels used by cracking furnaces. (Recent changes in the law have introduced additional requirements for the measurement of sulfur in waste gases going to flares. This will be commented more fully below.) Furnaces burn “fuel gas” which can be of varying composition. However, typically, fuel gas is considered to be as shown in Table I. The sample is usually dry with minimal contamination. The primary measurement issue is that the concentrations of the components can vary rather widely in their ranges.

TABLE I. REPRESENTATION OF TYPICAL FUEL GAS STREAM MATRIX		
COMPONENT	TYPICAL CONCENTRATION	MEASUREMENT RANGE
Hydrogen (H ₂) plus Methane (CH ₄ or “C ₁ ”)	80 – 90 %	n/a
Carbon Dioxide (CO ₂) and Ethane (C ₂ H ₆ or “C ₂ ”)	10-20 %	n/a
Propane C ₃ H ₁₀ or “C ₃₊ ”) and heavier	Balance	n/a
H ₂ S	low; see text	0-320 ppmv
Other sulfurs	Assumed very low	Ignored
Typical process conditions: Ambient to 80°C and at 20-80 psig (2-5.5 barg); may vary in some cases;		

The sample is readily accessible without unusual sample handling issues except that special care is required to avoid sulfur loss. (For example, ordinary stainless steel has an affinity for sulfur and H₂S will adsorb and desorb from the walls of tubing, valves and other materials in contact with it. This can dramatically and negatively affect the performance of the process analyzer system. Additionally, calibration samples must be of high quality and properly handled to avoid degradation and they are rather expensive. Note, while these topics are important to the analyzer, they have been addressed in the literature and are outside the scope of this paper.)

The required measurement range of the H₂S, as called out in the CFR, is 0-320 ppmv. (Note, this measurement range was formerly 0-300 ppmv under Subpart J.) Operators of furnaces are in violation of regulations if they exceed a nominal 50% of range or 162 ppmv. It is not a requirement to report exact concentrations if the span of 0-320 ppmv is exceeded, so all recording and outputs are required, specifically, to be scaled to that range. It is additionally not required that the actual concentration of the H₂S below 320 ppmv be highly accurate with respect to the reference method. The CFR requires Relative Accuracy Testing (RATA) on a periodic basis. The RATA test compares the results of the process analyzer with a concurrent analysis

performed according to Method 11 of the Code. Method 11 is a laboratory-style iodometric titration method involving wet chemistry.

As required in Performance Specification 7, the Relative Accuracy (RA) of the CEMS must be no greater than 20% when the average Reference Method (RM) value is used to calculate RA or 10% when the applicable emission standard is used to calculate RA⁽¹⁾. Method 11 is the former so the process analyzer can vary by as much as 20% relative to the laboratory validation method. For full compliance, a 2-point validation must be made daily to confirm the analyzer remains calibrated: approximately 80% of range or about 256 ppmv; and approximately 10% of range or about 32 ppmv are typical validation points. Assuming that a modern process analyzer has been correctly calibrated to a properly certified standard, the tolerance of $\pm 20\%$ Relative Accuracy is quite generous.

However, furnace operators often scrub fuels to a very high degree and operate much below the upper limit. It is not unusual to find typical H₂S concentrations at 5 to 10 ppmv and even lower. Furthermore, in these cases the operators may desire to know with some precision exactly what the H₂S measurement is and may desire to use the measurement to assist in controlling a sulfur scrubber providing the fuel. This can create a conflict of objectives and this topic is further discussed below.

The actual time required for analysis update is also not typically a problem for process chromatography. For CEMS compliance, fuel gas streams must typically be analyzed 96 times every 24 hours or one analysis every 15 minutes. Modern chromatographic methods require less than 5 minutes for the analysis and are well in conformance with this requirement.

CHROMATOGRAPHIC METHODS

The chromatography required for this analysis is relatively straight forward. Two techniques can be employed as described by the hardware and column application technique in Table II.

TABLE II. SUMMARY DESCRIPTION OF GAS CHROMATOGRAPHIC METHODS USED FOR MEASUREMENT OF H₂S IN FUEL GAS

	Detector Hardware	Column Application Technique
1	Flame Photometric Detector (FPD)	Column Valve Backflush to Vent
2	Thermal-conductivity Detector (TCD)	Heart-cut and Backflush

The following discussion describes these two methods and illustrates their relative advantages and disadvantages to the owner – operator. Note that the particular column separation techniques that are selected here for description are illustrative. In other GC implementations, there can be variations in valves, columns and hardware and even in the basics of the technique. However, the impact of these variations on the characteristics compared here is minimal; as will become clear, the basic requirements of any column techniques chosen are the same and are driven by the detector hardware of choice.

The FPD is a highly sensitive and selective detector that responds to sulfur but has a very limited response to hydrocarbons. By comparison, the TCD is a less sensitive but universal detector that responds to most components. In either case, the column application technique that is used must take into consideration these differences. On the other hand, it is these differences *including* their impact on column technique that leads to the comparison in advantages and disadvantages for the owner.

Figures 1 and 2 below are photographs of TCD and FPD hardware configurations, respectively. Figures in the next two sub-sections illustrate the oven hardware configurations and related column techniques. The application techniques described here employ 10-port chromatographic valves as illustrated. The same applications can be done with 6-port valves and by other means. Note, these chromatographic techniques are well known by persons skilled in the art. It is not the purpose of this paper to explain them in detail. However, the brief descriptions provided below will help clarify the subsequent comparison of characteristics.

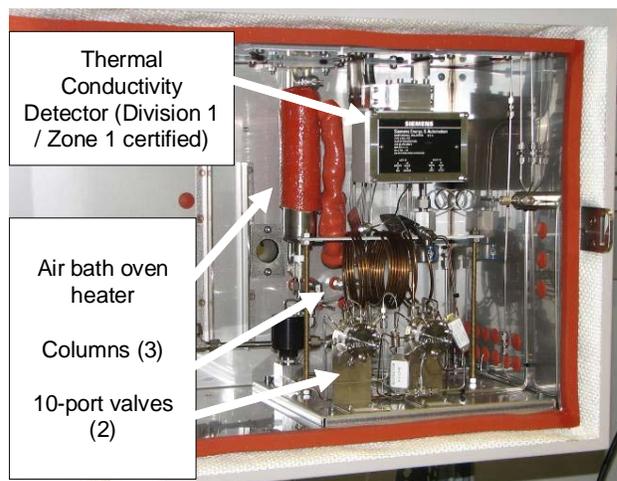


FIGURE 1. TCD HARDWARE CONFIGURATION

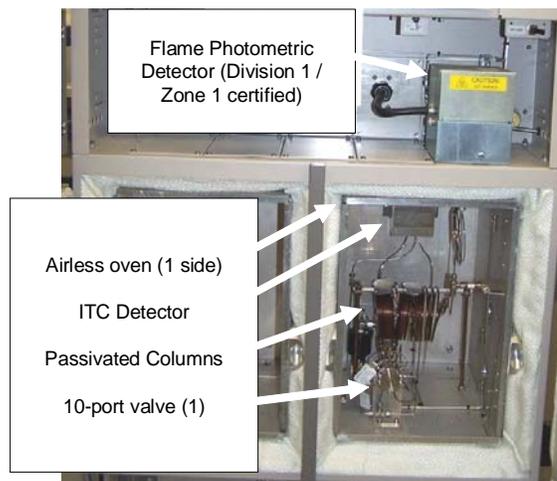


FIGURE 2. FPD HARDWARE CONFIGURATION

DESCRIPTION OF METHODS – FPD

The FPD is a selective detector. Ideally, this means that it would respond to the presence of sulfur but not to the presence of hydrocarbons. Therefore, it might seem that no chromatographic separation is required at all. However, in practice, the flame response of the FPD is affected by the presence of significant quantities of hydrocarbons and the response of the photo-optics is damped by quenching and other mechanisms. Therefore, it is necessary to separate the H₂S from other hydrocarbons. However, the degree of separation needed is not stringent so a relatively simple column system can be used.

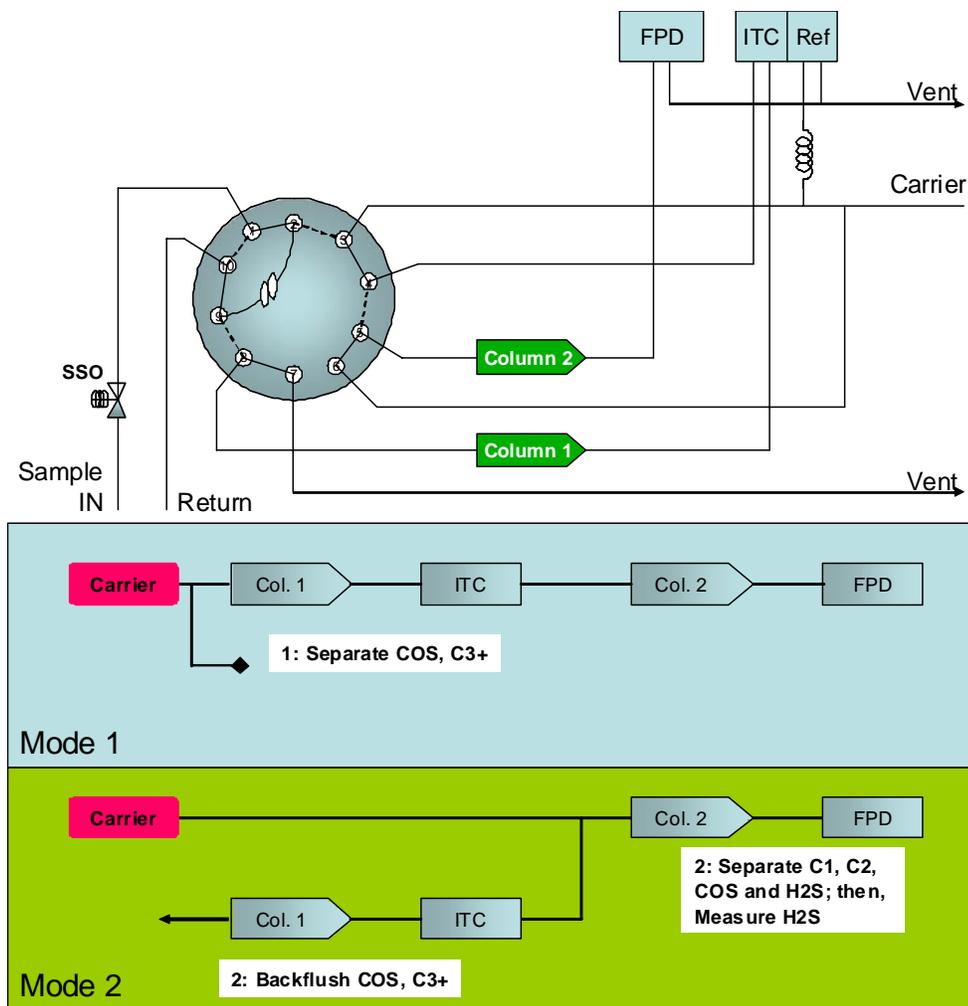


FIGURE 3. ILLUSTRATION OF FPD CHROMATOGRAPHIC METHOD.

As noted in Figures 3, the necessary separation can be achieved with two columns and a single 10-port valve configured as a column valve backflush to vent. Column 1 separates the lighter gases H_2 , C_1 , C_2 and H_2S from the heavier COS and C_3+ . Sufficient column length and appropriate flow are required for this separation only. The lighter gases are permitted to elute from Column 1 and pass on to Column 2. Then the valve is actuated which reverses carrier flow through Column 1, causing the COS and C_3+ which have not eluted to be flushed backwards to vent. Meanwhile, additional separation occurs in Column 2 which provides full separation between H_2 , C_1 and the C_2/H_2S pair and some partial separation of C_2 and H_2S . This minimizes the amount of hydrocarbons which elute concurrently with the H_2S to the degree necessary to prevent quenching or other dampening effects on the FPD signal. The FPD then provides measurement of the H_2S only.

The size of the injected sample is chosen to be as large as possible while keeping the measured H_2S output on scale. An FPD is extremely sensitive to sulfur-containing molecules so it is easy to select a sample loop size that will deliver a full scale H_2S peak. In fact, it is easy to make the

sample loop too large. According to the CFR, the measurement range must be limited to 320 ppmv; therefore, this becomes the factor which limits sample injection size.

(Note for reference, it is readily possible to use an FPD to measure H₂S in fuel gas at a range of 0-500 ppbv and with MDL as low as 10 ppbv! This would be about 640 times more sensitivity than is needed for the CEMS requirement. However, this low end performance cannot be achieved in the same configuration needed for the higher range CEMS application. This is commented further in later sections of this paper.) It is important here to note also that the natural response of the FPD is not linear; it responds roughly to the square of the quantity of the component present. For example, if the injected sample size is doubled, the response of the FPD is approximately 4 times greater. This characteristic amplifies the fact that detector response to H₂S is the limiting factor on sample injection size.

Note the actual performance of the chromatography is simple and non-critical. Column 1 must provide separation only sufficient to ensure that enough heavier components do not pass on to Column 2 where they may accumulate over consecutive cycles causing degradation of Column 2 performance. Additionally, Column 2 must provide only enough separation of H₂S from the hydrocarbons so as to avoid incidental negative impact on the operation of the FPD. Because sulfur compounds are the only peaks that can be observed, peak gating times may be adjusted quite wide permitting greater tolerance for operational changes over time. Tolerance can be 5 seconds or more. Both column separation requirements are easy enough that the exact time of valve operation is not critical; the window after H₂S elutes but before COS and C₃+ start to come out can be 10 seconds or more wide. (Note, of course, once a valve time is set up, it is assumed that run-to-run timing of the valve switch will not vary.) Figure 4 illustrates resulting chromatograms.

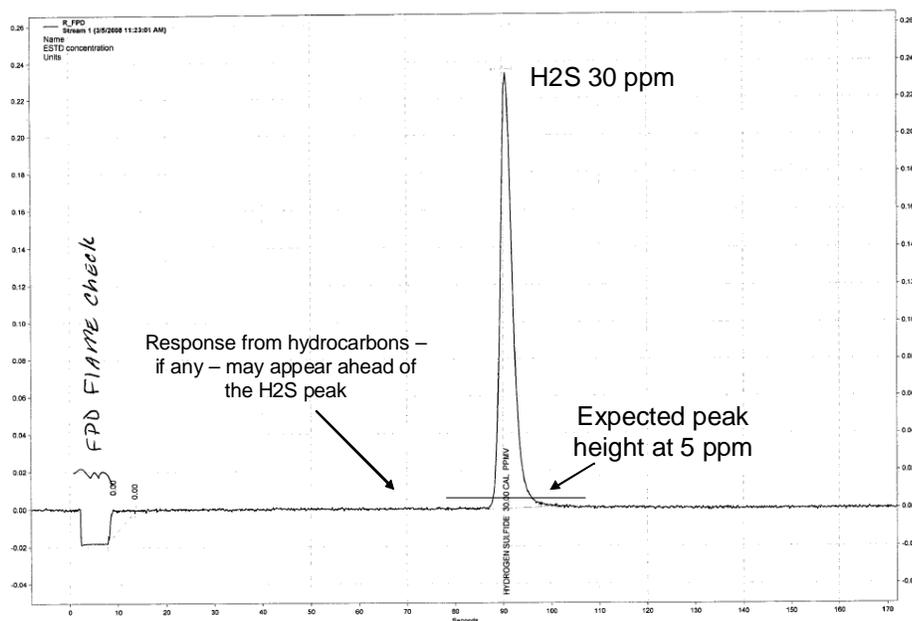


FIGURE 4. FINAL CHROMATOGRAM WITH FPD SHOWING H₂S AT 30 PPMV

These non-critical tolerances make maintenance and set up of the chromatograph very straightforward, and also mean that on-going maintenance required to adjust timing and gating is minimal. Furthermore, this translates into better repeatability and stability of the measurement output which in turn means more reliable long-term compliance with the basic CEMS objective.

DESCRIPTION OF METHODS – TCD

Figure 5 illustrates the oven piping configuration and column modes for a column application that works with a TCD. It can be seen immediately that the chromatography for the TCD is somewhat more complicated than for the FPD application described above. Since the TCD is a universal detector (that is, it is not selective to different compounds) the H₂S component must be fully and reliably separated from hydrocarbons and other compounds.

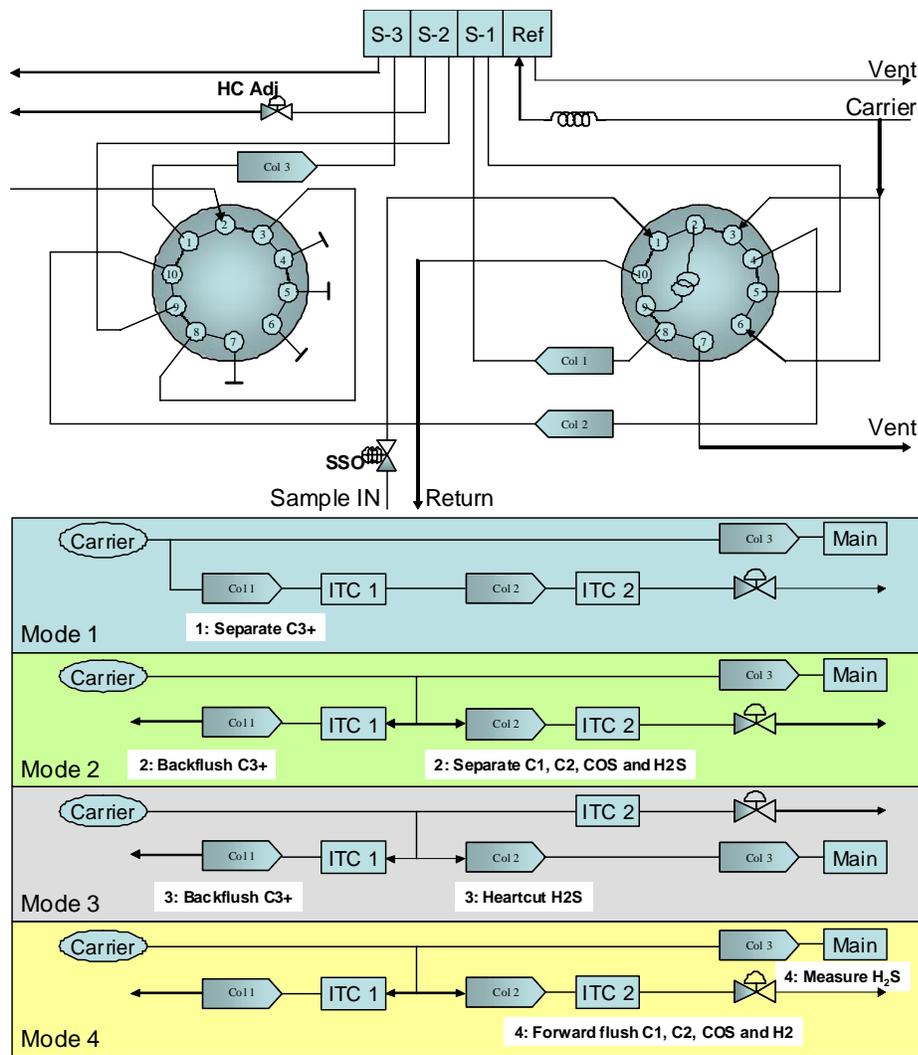


FIGURE 5. ILLUSTRATION OF TCD CHROMATOGRAPHIC METHOD

The H₂S and the C₂ components elute in a similar manner close to each other. Therefore, it may be observed that the separation of them is the primary chromatography problem. To solve this, three columns are used here in a Backflush and Heart-cut column arrangement.

As with the solution for FPD, Column 1 performs the task of separating for backflush the propane and any heavier components (C₃+) present. As before, Valve 1 is used to establish the Backflush Mode. It is possible to use literally the same column and chromatography set up for this purpose in either detector. However, some optimization is possible. If column cost is a concern, a less efficient column can be used in the FPD application.

For the TCD, Column 3 is more critical. It must provide much better separation of the H₂S and the C₂. (Note additionally, COS is separated here and may be observed if the heart cut window is widened.) This typically adds some cycle time and requires better performance because the heart-cut operation must be established. The heart-cut is needed because Column 2 is unable to separate H₂S and C₂ completely in a suitably short cycle time and with repeatable peak shape and characteristics.

Valve 2 is used to perform the heart-cut. The heart-cut valve is operated after the majority of C₂ has eluted but at some time before ANY of the H₂S begins to elute. (Note C₂ is diverted to vent.) The valve is left open, diverting the flow out of Column 2 onto Column 3 until after ALL of the H₂S has eluted. Then the valve is closed and the remainder of any hydrocarbons in Column 2 continues to elute to vent. Meanwhile, the entire H₂S peak and the residual, unseparated portion of the C₂ peak flow forward through Column 3 and are fully separated. The H₂S peak is measured as it passes by the TCD. The resulting chromatogram on the main detector is shown in Figure 6.

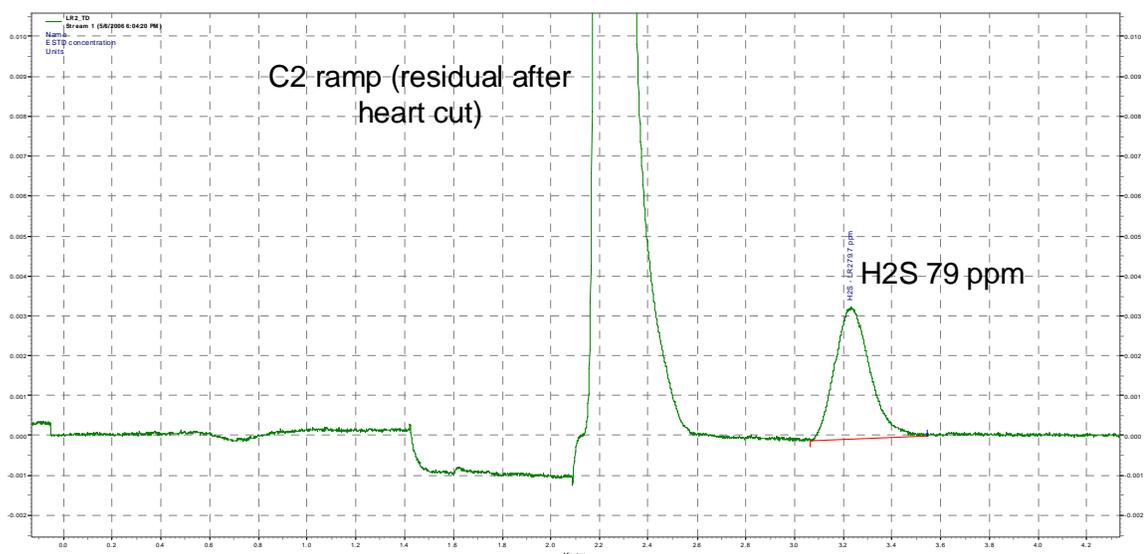


FIGURE 6. FINAL CHROMATOGRAM WITH TCD SHOWING H₂S AT 79 PPMV

The sample loop size in this application must be selected carefully. Because the TCD is not nearly as sensitive to sulfur compounds as the FPD, it is desirable to make the injected sample as large as possible. However, as the sample size is increased, the quantity of hydrocarbons injected onto the columns increases as well, ultimately flooding the columns and degrading separation. This is observed as peaks widen significantly and begin to have broad, flat tops.

In this application, if sample size is increased too much problems are observed as the C₃₊ peak broadens and Column 1 fails to separate it cleanly from the C₂ / H₂S peak. Eventually, it becomes not possible to set the backflush time properly with the result that some C₃ moves forward onto Column 2. Also as sample size is increased, problems occur on Column 2 when the C₂ component spreads and increases interference with H₂S. As this interference increases, it eventually becomes impossible to set the heart-cut properly which in turn can cause the separation performed in Column 3 to fail. The result is hydrocarbon interference with the measured H₂S which causes incorrect and non-repeatable results. The net result in the application is that the sample size is made as large as possible to achieve best reading on the TCD but not large enough to cause the problems noted here.

(Note, in this discussion, the effect of hydrogen in the sample is ignored. Hydrogen elutes ahead of methane. But if hydrogen carrier gas is used, the hydrogen component in the sample itself cannot be observed by the detector.)

The heart-cut operation must be set up correctly. The H₂S component, even at a full value of 320 ppmv is extremely small on the back side of the ethane (C₂) component peak after elution from Column 2. See Figure 7.

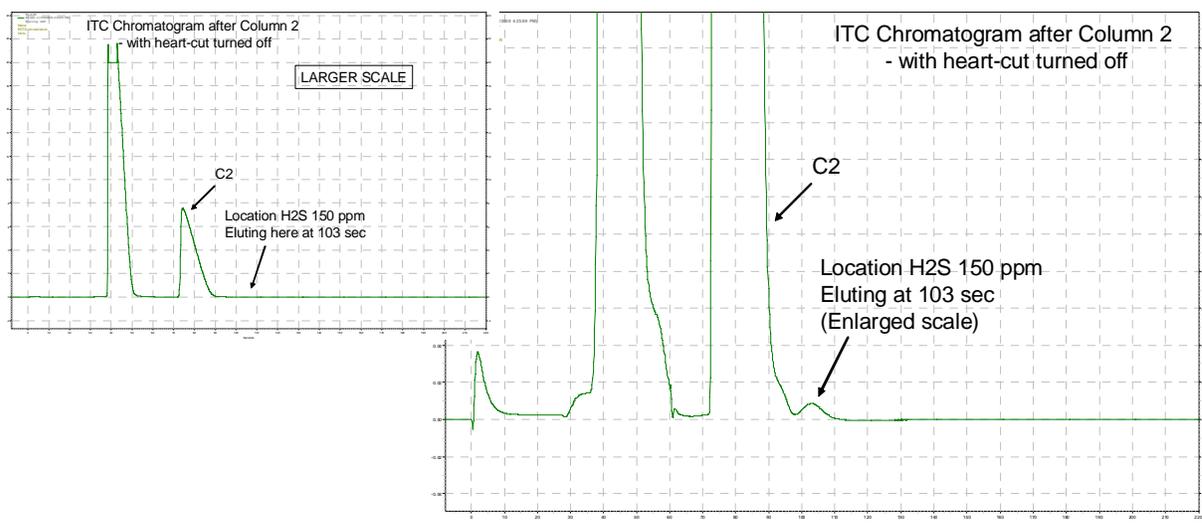


FIGURE 7. H₂S AT 150 PPMV, AFTER COLUMN 2 BEFORE HEART-CUT; ON TAIL OF C₂ ON TCD APPLICATION

It is difficult to set the front heart-cut valve switching time correctly to ensure that the entire H₂S peak is captured while getting as little as possible of the unresolved C₂ peak at the same time.

Furthermore, as the chromatography drifts over time, the maintenance of this valve operation time is important and must be checked regularly – even in the most stable of process analyzers. Finally, the repeatability of the performance of Column 1 and the stability and repeatability of Column 2 are of greatest importance to ensuring the long-term stability and results of the analyzer. Any variation in the elution times and flow rates of sample through those columns will result in a timing error on the operation of the front heart-cut.

Actually setting the heart-cut time requires patience and multiple runs. An inter-column detector (ITC) after Column 2 can be helpful to observe the activity at that point and to clarify the starting point when setting up the analyzer (Figure 7). But final set up requires trial and error; multiple runs must be made while adjusting the heart-cut time a little bit on each run and observing if there is an effect on the amount of H₂S that is measured. When the analyzer later requires field maintenance for any reason, this trial and error testing must be repeated to reestablish correct operation.

Backflush / Heart-cut column applications are relatively common in process chromatography. In an absolute sense, the technique is valuable and trained personnel can be expected to work with it successfully. However, as compared to the extremely simple application required for the FPD, it must be clear that the heart-cut technique is significantly more difficult to set up and maintain. This factor is important to consider particularly in critical CEMS applications.

As noted above, the limiting factor on sample size in the FPD application is that the extreme sensitivity of the FPD will cause the H₂S peak to go off scale on the required 0-320 ppmv reporting range. With the TCD, the limiting factor is that column performance does not allow the high concentration hydrocarbons to be separated adequately from the low concentration H₂S.

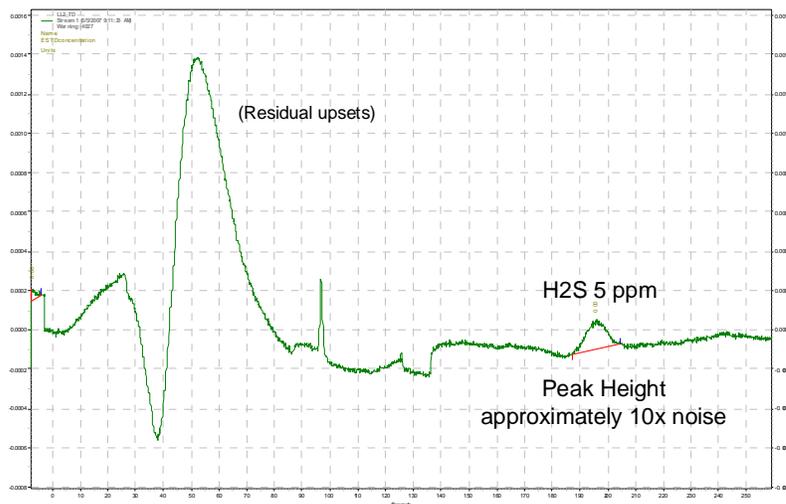


FIGURE 8. FINAL CHROMATOGRAM WITH TCD SHOWING H₂S AT 5 PPMV

(Note, thermal conductivity detectors used in modern process chromatographs can be used in applications with Minimum Detection Limit (MDL) as low as a few parts per million. Literature references noted in the bibliography here show applications of H₂S measurement as low as

1 ppmv in ideal conditions⁽²⁾. In general, in actual fuel gas applications, component MDL below 5 ppm can be achieved on measurement ranges of 0-100 to 0-200 ppmv. This may be seen in Figure 8.)

COMPARISON OF METHODS

So of the two chromatographic methods for doing the H₂S in fuel gas analysis, which should a process owner / operator choose? Clearly there are relative advantages and disadvantages to each of the methods. These will be discussed in the following categories:

1. Type of detector hardware and its impact on up-front costs and on-going maintenance cost
2. Chromatographic method and its effect on reliability, stability and on-going maintenance cost
3. Ability to use the chromatograph for control as well as CEMS purposes
4. Ability for the method to be adjusted to meet possible future changes in regulatory requirements

It can be noted that both techniques are well established in the industry in certified process installations. Therefore, the system designer does not need to worry about acceptability of the method, but instead needs to consider each of these factors regarding cost and suitability in the plant environment in which the system will be used.

DETECTOR HARDWARE

The detector hardware used in the two methods is significantly different. The TCD is generally very simple, involving a thermally sensitive element in a small volume cell (Figure 9). Two cells (commonly) are used; one provides a thermal reference against flowing carrier which is compared to the thermal signal from a second sense element. The detector is universal in that any vapor compound will affect the temperature of the sense element. The degree to which the elements are affected is proportional to the relative thermal conductivity of the particular compound as compared to the thermal conductivity of the carrier gas. This means, for example, that the detector does not respond to a separated gas which has the same thermal conductivity as the carrier since there is no thermal difference. In this application, that means that hydrogen carrier will preclude any response to the hydrogen content of the fuel gas.

The sense element itself can be a thermistor bead or conductive material. The response of the detector is highly linear over several orders of magnitude. The limiting factor at low signal levels is signal-to-noise ratio (S/N). The noise is a result of thermal activity and gas flow variations over the sense element and electronics. One definition of Minimum Detection Limit (MDL) is that the component peak is at least 2 times larger than noise⁽⁵⁾. Actual MDL for any given component is therefore dependent on application conditions. In a fuel gas application, as

noted above, MDL is below 5 ppmv. Note the Minimum Quantifiable Level (minimum concentration for which repeatable and useful measurement is possible) is 5 times larger.

These detectors are relatively inexpensive and essentially fool-proof. They require no special maintenance. Historically, thermistor elements can be damaged by hydrogen carrier. But this problem has been resolved in modern designs. No special utilities are required and no power or special controls are needed. Typically, the sensor elements will operate in the field for 3 to 10 years, depending on design and other qualities.

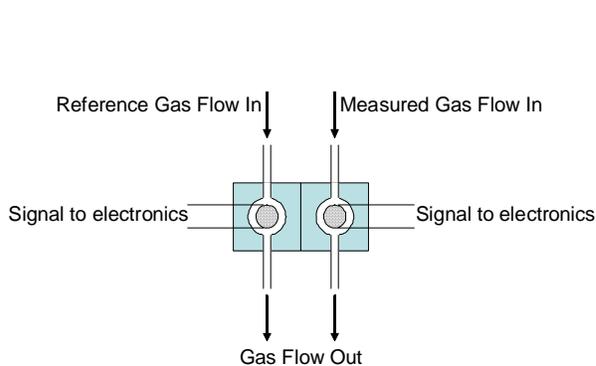


FIGURE 9. TCD FUNCTIONAL ILLUSTRATION

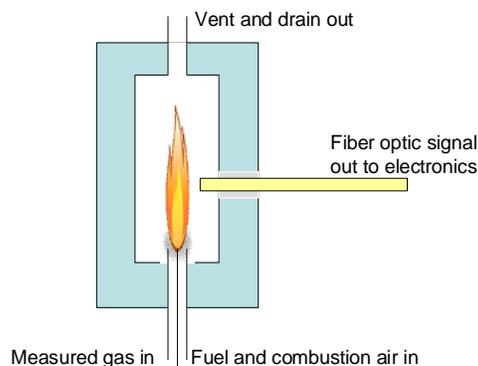


FIGURE 10. FPD FUNCTIONAL ILLUSTRATION

The FPD is a more complex detector (Figure 10). A flame is used to excite the component being measured in a fuel-rich environment. The excited sulfur atoms release photons upon recombining into S_2 molecules which are observed, via a fiber optic connecting cable, at a photomultiplier tube and amplifier. Any element which will excite in the flame can also be observed to one extent or another. To minimize this, an optical filter specific to the wavelength of the sulfur photons is used. This selectivity on photon wavelength makes the detector excellent for the fuel gas application since the only component to which the detector will respond to ideally is the sulfur compounds. There is, however, a limitation to this. The presence of hydrocarbons in the flame does, directly, affect the flame itself and creates relatively large quantities of CO_2 when they are burned. This suppresses (quenches) and otherwise affects the response of the flame to the sulfur. Therefore, chromatographic separation is used to remove the large bulk of hydrocarbons away from the sulfur. However, it is not critical that all hydrocarbons be removed.

Because the FPD has an active flame, it requires maintenance and it consumes additional utilities which are combustion air and hydrogen fuel. The air to fuel ratio must be properly adjusted to ensure correct flame performance. There must be a mechanism to detect loss of flame and to ignite it. If the flame goes out for any reason, there may be a change in the operation of the detector or its stability when the flame returns. Additionally, the flame chamber is physically larger than a TCD cell so there is more surface area that can affect or absorb and desorb sulfur. The actual geometry of the flame chamber, the burner tips, the light pipe connection and other features affect the performance of the detector; therefore there is a greater cost in the design and production of the system.

Previous literature⁽³⁾ has placed the incremental total 15-year cost of ownership of an FPD at \$160,000. This may be too high if today's better FPD systems are considered. For example, the reference has placed utility costs at \$6,000 per year above a TCD (\$10,000 versus \$4,000.) By comparison today, with one modern FPD design (example, Siemens Maxum FPD2), the actual utilities, incremental to a TCD, are H₂ fuel flowing at 100 cc/min and combustion air flowing at 75 cc/min. Assuming \$100 cost for a standard cylinder of ultra-high purity H₂ fuel and the same for purified air, this will translate into 9 bottles per year of each and \$1,800 in total cost of utilities per year compared to the \$6,000 noted. Furthermore, the air cost is often avoided or reduced if instrument air is used after passing through an air treater system. Of course, added to this would be the actual cost of manpower required to monitor and change out the bottles when needed. But even this added cost may be incrementally small if considered as a part of the normal activity of analyzer technicians who are already routinely checking and changing a large number of other utility gases used in a complete analyzer system.

Similarly, for example, current estimates of annual technical maintenance per year are expected to be much lower than the \$8,000 cited in the reference⁽³⁾. Today, it would be expected to total not more than 20 – 40 hours per year. At \$100 per hour, this would be a cost of \$2,000 to \$4,000. In other respects, the reference remains valid. For example, the incremental purchase cost cited (\$10,000 incremental) remains valid. Also, the spare parts cost estimate as cited (\$1,000 incremental) remains reasonable at this time.

In total, it might be reasonable in many situations to reduce the total 15-year costs noted in the reference by as much as \$50,000 to \$100,000. But regardless of such adjustments, it is still correct to conclude that an FPD costs more to operate for 15 years than a TCD.

CHROMATOGRAPHIC METHOD

The second point for consideration is that the chromatography itself is more complex for a TCD solution than for an FPD. The differences in chromatography have been described above. The technique used with an FPD is a very simple backflush configuration with valve and gate timings which have several seconds of tolerance for set up. The technique used with the TCD is a more complex backflush and heart-cut configuration in which valve and gate timings must be set somewhat more carefully.

The point was made above that heart-cut configurations are common and that competent maintenance personnel can expect to operate and maintain them successfully. However, the incremental time for maintenance of a heart cut as compared to maintenance of the non-critical backflush is larger. The degree to which it is larger is indeterminate and will vary widely according to the skill and experience of personnel involved.

(The exact increase is not significant to the point to be made below in this paper. But, for illustration purposes, one might compare only the 180 second FPD cycle time (Figure 6) with the 260 second TCD cycle time (Figure 8) and assume that 3 test cycles must be run when the FPD is maintained and 4 must be run for the TCD due to the greater set up complexity of the heart cut.

If one then compares only cycle run times ($180 \times 3 = 560$ seconds versus $260 \times 4 = 1040$ seconds) the comparison indicates that TCD application maintenance would take twice as long as FPD application maintenance. If one assumes \$100 per hour in technician costs and as little as 10 versus 20 hours per year in labor, the difference would be significant over the life of the analyzer.)

Furthermore, it is clear that in the event of a breakdown or actual column or valve replacement requiring that the chromatograph be completely set up from scratch, the time required for the TCD configuration will be at least 4 times longer than the time required for the FPD configuration. This difference is related to: a) the longer TCD cycle time; and, b) the need for multiple trial-and-error runs to confirm correct timings.

Again, the actual cost numbers provided in this and the previous sections are not claimed to be actual but are illustrative. Actual numbers can be estimated by the chromatograph owner based on his own previous experience. However, the point made is that the cost difference could be significant and should be considered in the selection of a particular GC technique.

CEMS AND CONTROL

The primary reason that hydrocarbon processors buy a sulfur in fuel gas chromatograph is to meet regulatory demands to monitor environmental impact. However, as has been noted previously, many process owners use sulfur scrubbers to remove sulfur from the fuel they are about to burn. Therefore, the normal concentration of the H_2S in the fuel actually can be very low. It is not uncommon to find fuels that contain less than 10 ppmv H_2S as their normal condition.

In these situations, the owners may have a second objective that arises and that is to use the H_2S monitor for purposes of control, or at least limit checking, on the sulfur scrubber. The desire is to reduce total cost of analyzers.

However, this is a conflicting objective to the original. A CEMS is concerned about high concentrations that break through an upper control limit. The government does not care about repeatability, stability or accuracy that is better than is stipulated in the regulations. As described above, these requirements, $\pm 20\%$ relative, are not stringent. Control, on the other hand, requires good stability and repeatability. Most control applications want measurements to repeat within 1% or better. In low concentrations such as this, that tolerance may be relaxed to $\pm 3\%$ to $\pm 5\%$. But in any case, it is more stringent than CEMS requires.

The problem, for the process analyzer, is the difference in range. It is common that the control application would like to monitor H_2S on a typical operating value of less than 10 ppmv. In ideal circumstances, it would then be best to scale the analyzer for a range of 0-20 ppmv. Of course, this is not allowed by the CEMS requirement.

Therefore, a point of comparison that now will be made is the performance of the two chromatographic methods at low concentrations even though the range remains set at the regulated point of 0-320 ppmv.

A chromatogram was provided above (Figure 8) from a TCD configuration being used to measure a 5 ppmv H₂S component in fuel gas. The range has been set at 320 ppmv and the analyzer is certifiable for CEMS. As can be seen, the peak is clearly discernable and well above the MDL. Nevertheless, the noise level is significant and the actual performance of this particular test unit was a repeatability of greater than $\pm 5\%$. The owner considered that level as being marginal for control purposes.

Figure 4 above provides a chromatogram from a FPD application. The actual peak shown is 30 ppmv which is clear and repeatable. However, if the concentration is dropped to 5 ppmv, the detector response will drop by a factor of 36. (The response is the square of the concentration.) In that case, the FPD signal is very near noise levels and performs in a manner that is comparable to the TCD. An estimated peak height is shown in the figure.

In other words, neither application is particularly good for control on a 5 to 10 ppmv component.

However, the question may then become: what else can be done? One answer (setting system complexity aside) is to provide for multiple ranges. Since the analysis cycle time of either method is less than 5 minutes and the regulations allow 15 minutes, it is possible to configure modern chromatographs with two sample valves and run the analysis on 2 different ranges. (Obviously, this adds complexity to the overall system which may be unacceptable for other reasons. The solution is suggested here only for comparison purposes.) However, if this is done, what performance can be expected?

To make the range smaller, it is necessary to increase the sample size. In the case of the FPD, this can be done directly. As the sample size is increased, the hydrocarbons will flood the first column and eventually the C₃+ peak will fail to separate from the C₂/H₂S pair making it impossible to set the backflush time. However, the necessary sample size is reached long before that point. Separation in Column 2 is less a concern because the FPD has a lower sensitivity to the hydrocarbons present. Therefore, the FPD application can be set for a range that is substantially lower without difficulty.

However in the case of the TCD, it is not possible to increase the sample size very much. This is because it is necessary to maintain clean chromatographic separation at all ranges. As the sample loop size is increased, the separation in Column 2 quickly becomes a problem. It is estimated that a range of 0-200 ppmv could be achieved, but not lower.

Note also that control needs can be met in some particular commercial analyzers by duplicating the entire column application and detector inside the original oven. This permits the original CEMS application and the additional control application to run completely separately and independently. This kind of arrangement can meet the goal of cost savings without compromising the original measurement objective of either the CEMS or control needs.

FUTURE REGULATORY CHANGES

There continues to be discussion in the industry, especially in California and certain other areas, about the possibility that the Federal Regulations may require further reductions in sulfur. Ranges as low as 0-50 ppmv have been mentioned. (Note, at this time no actual changes are known to be pending.)

Also currently under discussion are regulations that will call for inclusion of Total Reduced Sulfurs (TRS) consisting of H₂S, COS and CS₂. These regulations are already included in portions of Subpart Ja but are stayed in court. However, if these are eventually implemented it is clear that the concentrations of other sulfur components would be lower than the typical concentration of H₂S. This may increase the complexity of the chromatography and require greater detector sensitivity.

A related regulation now in effect in California, SCAQMD Rule 1118⁽²⁾, calls for monitoring sulfur in waste streams going to flares. This application has some similarities to the fuel gas application but is quite different over all. The concentration of fuel gases, while subject to change, is nevertheless relatively constant. The background gases in flare streams however can change widely from 0 to 100% and can include many more and different hydrocarbons. This makes the chromatographic separation much more difficult.

Any changes or broadening of the application are likely to require lower ranges or have more severe chromatographic requirements. At the present time, such changes will be more readily accomplished with the FPD configuration. As noted previously, the TCD application is limited only in part by the sensitivity of the detector itself. In fact, modern TCDs have greatly improved sensitivity as compared to older systems. However, the TCD application is limited by the chromatography in combination with the lower sensitivity. When measuring sulfurs, the FPD has greater inherent sensitivity; but of equal importance is the fact that its selectivity allows simplification of the chromatographic separation.

It can be noted that there is also current discussion about requiring the measurement of other non-sulfur components including benzene. Such a requirement would also bear on the selection of the measurement method and the particular equipment that is used for the measurement. However, that discussion is outside the scope of this paper.

OTHER PERFORMANCE NOTES

Other characteristics of the two applications are compared in Table III.

TABLE III. COMPARISON OF PERFORMANCE CHARACTERISTICS OF CHROMATOGRAPHIC METHODS		
Characteristic	FPD	TCD
Carrier gas requirement	Helium or Hydrogen	Hydrogen
Cycle time with Hydrogen	3 - 4 minutes	5 minutes
Dynamic range and response of hardware with test component in carrier gas	2-3 orders of magnitude; response varies as the square of quantity; linearization required in electronics	Up to 5 or more orders of magnitude; response linear better than 5%
Measurement range of H ₂ S in fuel gas application	~5 – ~400 ppmv (in CEMS application, upper range must be restricted)	~5 ppmv – ~2% (in CEMS application, upper range must be restricted)
Sample size limiting factors	Upper range is limited by largest sample that will keep 320ppmv peak on scale; Lower limit is then limited by S/N due to square response of detector	Upper range is limited by largest sample that will avoid column flooding and loss or column separation performance; Lower limit is then limited by detector S/N
MDL of H ₂ S in carrier	~ 1 pp billion	~ 1 pp million
Possible MDL of H ₂ S in fuel gas; assuming chromatographic method is optimized	5 – 10 pp billion	2-5 pp million
Minimum Control Limit of H ₂ S in fuel gas (< 5% repeatability)	5 ppm	5-10 ppm
Drift over 1 month	< ±2%	< ±2%
Validation	2 points	2 points

SUMMARY OF COMPARISONS AND CONCLUSIONS

The following points are a summary of issues described above:

1. Either an FPD or TCD chromatographic application can meet the objective of a Continuous Emissions Monitoring System for H₂S in fuel gas.
2. The FPD hardware has a somewhat higher front-end cost and a somewhat higher on-going cost of operation and maintenance than the TCD hardware. This higher cost is a result of a more complicated detector and utility gas consumption.

3. The TCD application has a somewhat higher front-end cost and a somewhat higher on-going cost of maintenance than the FPD application. This higher cost is a result of higher chromatographic complexity including additional valves, columns, set-up time and cycle length.
4. Both applications and detectors equally constitute only one part of the total CEMS solution. Significant design care must be given also to sample transport, handling and conditioning, calibration methods, data logging and regulatory compliance certification.
5. Both applications – when configured primarily for their primary goal of meeting CEMS objectives – perform about equally at very low end of the 320 ppmv CEMS scale. That is, repeatability and performance that might be required for example for control at less than 10 ppmv is comparable.
6. When multiple ranges or redundant applications can be used, the FPD application can most readily be extended to lower levels of detection. Because of this ability, the FPD application is most amenable to changes which might make it useful for other related very low concentration sulfur applications should that become desirable in the future. In particular, any application which might require further speciation of sulfurs besides H₂S can best be done with the FPD.

In conclusion, it is clear that gas chromatography remains a powerful and versatile tool for measuring H₂S in fuel gases for purposes of monitoring compliance with environmental protection requirements. Advances in gas chromatography techniques continue to strengthen this tool. Two viable methods exist which employ different hardware and different chromatographic techniques. Some of the points of comparison for selecting which of the two methods should be used have been described. Actual selection for a given plant installation should be made giving consideration to these points and how they are modified by the experience and conditions of the individual plant.

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