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Abstract: Focuses on exhaust gas analyzers that are computer-controlled and fully integrated for measuring major components in engine exhaust. Use of gas analyzers as emission machines by automobile repair shops; How exhaust gas analysis can lead to a more accurate diagnosis of most driveability problems; Use of stoichiometry as a description of the perfect air/fuel ratio; Measurement of hydrocarbon emissions.

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ANALYZING EXHAUST GAS READINGS**What comes out the pipe tells a tale.**

Exhaust gas analyzers have been in the shop since the 1940s. Those early instruments measured electrical conductivity of the exhaust stream, which only gives an indication of a rich or lean air/fuel mixture. Not many mechanics even knew these meters existed, and most simply 'measured' air/fuel mixture at idle with their nose.

By the mid-1970s, mixture specs were given in percent carbon monoxide (CO), and the tailpipe probes were connected to real (though limited) gas analyzers. At that time, mixture was the only thing being measured, and even the most sophisticated fuel injection systems only had a few analog sensors. The word 'emissions' was rarely used outside the lab, and the word 'driveability' hadn't been invented yet.

But things changed fast and by the mid-'80s, some shops built their whole business on 'tune-up' work, using huge, console-style diagnostic centers with four-gas analyzers. These machines were truly useful diagnostic tools, but there weren't many techs using them. Today, emissions regulations and driveability have a major impact on daily life in the shop, and exhaust gas analyzers are used almost every day in shops that have one.

The latest machines are computer-controlled and fully integrated systems for measuring either four or five major components in engine exhaust. Many shops that own a gas analyzer probably call it an emissions machine, because they use it almost exclusively for emissions inspections. For driveability or emissions problems, most technicians are more likely to rely on a scan tool and their own experience, rather than spend time using the exhaust analyzer. But knowing what's coming out the tailpipe can tell you almost everything that's happening between there and the air filter. With a little practice, exhaust gas analysis can help lead to a more accurate diagnosis of most driveability problems.

Five-gas analyzers show the concentration of carbon monoxide (CO), hydrocarbon (HC), carbon dioxide (CO₂), oxygen (O₂) and oxides of nitrogen (NO_x). Knowing the level of these components in the exhaust can tell you what happened inside the combustion chamber, but there's one important detail to keep in mind. Unless otherwise specified, all exhaust gas readings are taken at the end of the pipe, after the catalytic converter has modified the engine-out exhaust. If you're in doubt as to the effectiveness of the catalyst, you'll need to gather some additional data before interpreting tailpipe numbers. Some imports have a pre-catalyst tap, and there are adapters that make it possible to take a pre-catalyst reading on almost any car. This can be useful information. But emissions specifications are tailpipe numbers and most of the scientific data we found while researching this article is reported as tailpipe readings. So let's get started.

Stoichiometry

We've all seen the word stoichiometry used as a description of the perfect air/fuel ratio, but the true definition is rarely explained: It describes the conservation of mass in a chemical reaction. No matter how a pound of air/fuel mixture is processed in the combustion chamber, what comes out of the exhaust port is still a pound of something. Because we want all the fuel in the chamber to burn (convert to something else), we need to make sure there's enough oxygen to react with all of it. Every hydrocarbon molecule that burns completely will react with an exact number of oxygen molecules, but air is only 21 percent oxygen. In order to burn the fuel completely and get all the power it can provide, there must be enough oxygen molecules to react with each atom of hydrogen and each carbon atom.

For an internal combustion engine, stoichiometry means getting exactly the right number of oxygen molecules into the chamber to react with each hydrocarbon molecule. Without going into the math and chemistry, it's enough to know that for a piston engine running on gasoline, it takes a minimum of 14.7 pounds of air to get enough oxygen to completely burn each pound of gasoline. Under certain conditions, it's possible to run with an air/fuel ratio as lean as 18:1, or as rich as 12:1, but these present other problems we'll describe later.

Hydrocarbon emissions

Fuel is hydrocarbon, so any HC in the exhaust gas is unburned fuel. When hydrocarbons are completely burned (combined with oxygen), they become CO₂ and water (H₂O). At idle, a tailpipe HC reading of 50 ppm is acceptable, but that's downstream of a fully functioning catalyst. Even with a perfect air/fuel mixture and today's near-perfect combustion chamber designs, some of the fuel is still able to 'hide' from the flame in the chamber, and engine-out HC emissions (pre-catalyst) may be as high as 500 ppm at idle.

These engine-out hydrocarbon emissions can be cleaned up by providing enough heat and oxygen outside the cylinder to complete the burn. Injecting fresh air immediately after the hot exhaust port will work, which is how HC emissions were reduced before catalytic converters were needed to meet tighter 1975 emissions standards. An increasing number of newer cars have an electric air injection reaction (AIR) pump that runs immediately after cold-start to burn engine-out HC emissions before the catalyst is warmed-up. Once it reaches operating temperature, today's catalytic converter is often so efficient that the analyzer might not even get a hydrocarbon reading at idle.

When HC emissions are high at the tailpipe, that can mean one of three things: Either the catalyst is not functioning, the air/fuel mixture is not correct or the fuel is not burning properly in the combustion chamber. The easiest first step in diagnosing high HC

emissions is to measure the temperature of the catalyst inlet and outlet pipes with an infrared thermometer. If there's no temperature difference with everything fully warmed up, the catalytic converter isn't working. At idle, the outlet temperature should be at least 10 percent higher than the inlet.

Assuming the catalyst is working and HC is high, we're left with incorrect mixture or misfire. It is possible for the air/fuel ratio in all cylinders to be so rich that HC is high at the tailpipe. This could be caused by a simple mechanical problem like a leaking fuel pressure regulator, or the powertrain control module (PCM) might be driving the mixture rich due to a faulty engine coolant temperature (ECT) sensor or a stuck-open thermostat. Whatever the reason, a rich mixture also would cause high CO and possibly high catalyst outlet temperature, but high CO and HC emissions still can happen even when the fuel injection system works properly, for example if the engine is burning oil.

If only HC is high, look for a reason the PCM might force the mixture so lean that it causes intermittent misfire. A steady miss with proper air/fuel ratio also will cause high HC. A bad plug wire, incorrect ignition timing, a vacuum leak or a mechanical problem that causes low compression can prevent the fuel from burning properly in the cylinder. A cylinder that's getting fuel but constantly misfires will not only send raw fuel down the pipe, it also may cause the PCM to enrich the mixture in the other cylinders because it detects the unused oxygen from the dead cylinder. A miss like this can cause serious overheating in the catalytic converter. The PCM in the later Porsche 928 measures temperature at each exhaust manifold and will shut down the injectors on the cold bank to prevent pumping raw fuel into the catalyst. Whatever the cause, high HC-only emissions usually indicates a lean misfire, an ignition failure or an engine mechanical problem.

Carbon monoxide emissions

Carbon monoxide is a relatively unstable gas that easily converts to CO₂ with just a little extra oxygen and heat. When the engine is running properly (at stoich), engine-out CO emissions are typically about 0.5 to 1.0 percent. With air injection or a catalyst, it's possible to reduce CO all the way down to zero at idle, but only when the engine is running properly.

If the air/fuel ratio is even slightly richer than stoich, CO will increase quickly. Above 1.0 percent engine-out CO, even the most efficient catalyst can't keep up, and catalyst temperature and tailpipe CO will increase even if HC does not. So a high CO reading by itself means the engine is running rich. Problems with the fuel injection system such as high fuel pressure or a bad coolant temperature sensor are obvious possibilities, but a dogged air filter, dogged PCV system or gas in the oil also can cause high CO emissions.

Carbon dioxide emissions

CO, HC and NO_x emissions are regulated by the federal government, and while CO₂ causes its own particular problems with the environment, it's not regulated. The level of CO₂ concentration in engine exhaust is a direct measure of combustion efficiency, so a high level is better. When the engine is running at stoich, CO₂ will peak at about 12 to 15 percent. When running either rich or lean, engine-out CO₂ will decrease. If it's below about 12 percent at the tailpipe, look for other readings that indicate the engine is running rich or lean. Remember there are two places that CO₂ is produced: in the combustion chamber and in the catalytic converter. If CO₂ is low but CO and HC readings are normal, look for an exhaust leak.

Oxygen

The level of oxygen in engine exhaust is inversely proportional to the CO₂ level: as one goes up, the other goes down. Earlier, we described stoichiometry as conservation of mass. So, to convert all the fuel and air into the gases we want, there must be enough oxygen to combine with every hydrocarbon molecule.

In a combustion chamber, a perfect mixture can only be accomplished if the chamber is a perfect sphere. That way all the fuel and oxygen molecules can 'find' each other, allowing all the oxygen and fuel to be converted in the burn. A piston engine combustion chamber can't be a perfect sphere, and there are many places for fuel molecules to 'hide' from the oxygen molecules.

To minimize HC emissions, there needs to be just a little extra air to make sure all the fuel can find enough oxygen. That means our 14.7:1 air/fuel ratio is actually just a bit lean of perfect, and engine-out oxygen level will be 0.5 to 1.5 percent. It's just as well because the catalyst can't convert CO and HC without oxygen. The engine can still run well with a considerably leaner mixture, and AIR or a simple catalyst can easily convert most CO and HC emissions even when the engine is run at 16:1. But with extra oxygen in the chamber, NO_x increases dramatically, and even the best catalyst can only reduce NO_x when the air/fuel ratio is very tightly controlled.

A normal tailpipe oxygen level will be no more than about 1.2 percent and may be as low as zero. Be careful of a zero reading though. It can mean all the oxygen was used in combustion/conversion, but it also can mean the engine is running rich. If that's the case, low or zero oxygen will probably be accompanied by high CO. A high oxygen reading can mean the engine is running lean, but there would be other indications, too. If CO, HC and oxygen are all high, suspect a failed catalytic converter. A high oxygen reading by itself can mean a leak in the exhaust system. An oxygen reading is most useful when compared with the CO₂ reading: as one goes up, the other goes down.

NOX emissions

We left this discussion for last because if you can read the other four gases, measuring NO_x emissions isn't really necessary for diagnosing engine performance. It is a regulated emission, but the only way to get a legally valid reading in many areas is with the engine under a controlled load on a dynamometer. All that said, NO_x readings at idle can still provide useful information.

NO_x is a chemical bonding of nitrogen and oxygen. Under normal atmospheric conditions, nitrogen is a stable, inert gas; it won't bond with anything. But under the high pressure/temperature conditions inside a piston engine, nitrogen will readily combine with oxygen to form nitrogen monoxide (NO). By itself this is bad enough, but it's not stable and once released into the air it will bond with another oxygen molecule to form NO₂. This is a very toxic gas that mixes easily with moisture in the air to form nitric acid. NO_x is the most difficult of the three regulated emissions to convert, although if engine-out levels are low enough, a properly designed catalyst system is quite effective.

High NO_x is caused by high oxygen levels and/or combustion chamber temperature. Engine-out NO_x is controlled with extremely precise management of the air/fuel ratio and by reducing combustion chamber temperature with EGR or long valve overlap. A normal

NO_x reading should be no more than 100 ppm at idle and no more than about 1,000 ppm at a steady road load. If the engine is running lean, has advanced ignition timing or some problem that causes high coolant temperature, NO_x increases drastically, and even the best catalyst or EGR system can't keep it in check. Carbon deposits that increase compression or cause hot spots also can increase NO_x, and an engine that pings will always have high NO_x. When all is right with the engine, high NO_x readings usually indicate a failed catalytic converter.

Catalytic converter

A catalyst is something that enables or speeds up a reaction without itself being changed in the reaction. In an automotive three-way catalytic converter (TWC), the catalyst includes platinum group metals (platinum and rhodium) and other metals and base materials. The catalyst converts the three gases that are regulated emissions: CO combines with oxygen to become CO₂; HC combines with oxygen to become CO₂ and H₂O; and oxygen is stripped away from NO_x. That's two different functions in one component, oxidation and reduction.

Today, most converters are monolith types, with the appropriate chemical coating baked onto honeycomb ceramic blocks or rolls of corrugated metal that the exhaust gas flows through. Earlier converters had two separate monoliths in one can: the front block coated with a NO_x reduction catalyst, and the rear block coated with an oxidation catalyst. These also are known as selective or dual-bed catalytic converters.

It makes sense to have the reduction catalyst up front because it liberates oxygen that can be used by the rear oxidation catalyst, but it's not enough. There are two ways to get the additional oxygen needed for the oxidation phase. Earlier engine management systems used AIR to supply air to the exhaust ports and/or directly to the catalytic converter. But that was before catalysts were used to meet tighter NO_x emissions regulations. As noted previously, an electric air pump is used on some of today's vehicles, but it supplies air only after cold-start for quick catalyst light-off.

To achieve high conversion efficiencies in modern three-way catalysts, today's engine management systems constantly switch air/fuel ratio within an extremely tight range that extends just a few tenths of a point rich and lean of 14.7:1. The lean phase provides the extra oxygen for the oxidation bed, and the rich phase allows the reduction bed to 'catch up' with the NO_x emissions. During the lean phase, oxygen is actually stored by one of the chemicals in the catalyst coating, then released during the rich phase. This balancing act works well, but only when the rich/lean switching happens at the designed speed. A gas analyzer is too slow to see it happening, even when looking at engine-out emissions, but the signal from a healthy O₂ sensor shows the rich/lean switching quite well.

The catalyst efficiency monitor in OBD II systems actually looks at the oxygen storage capacity (OSC) to determine the ability of the catalyst to convert HC. As catalyst efficiency deteriorates, its OSC is reduced and the switching rate of the rear O₂ sensor will increase.

When the rear and front sensor switching rates reach a pre-programmed ratio of about 0.75:1, the catalyst is considered failed. With a good preconditioning run, CO and HC conversion may be restored for a short period, but NO_x will still be high. A gas analyzer that reads NO_x can provide a fairly reliable indication of a failed catalyst.

One way to learn more about gas analysis is to pull a vacuum line or disable an injector, spark plug or sensor on an engine that's running properly and watch how the readings change. No matter how much experience and proficiency you have with a scan tool, there are times when a gas analyzer is the only way to get a complete picture of how the engine is running. Electronic signals can tell you what the computer is seeing or doing, but a properly calibrated gas analyzer doesn't lie, and sometimes those readings are the only way to tell what actually happened in the chamber.

Our thanks to Johnson Matthey, Andros Technologies and Paul Baltusis, OBD technical specialist at Ford Motor Co., for providing some of the information and research material that made this article possible.

CHART: This stoichiometric chart shows engine-out emissions at various air/fuel ratios in a gasoline piston engine.

CHART: This chart illustrates engine-out and tailpipe emissions as a function of air/fuel ratio. NO_x is the most difficult to convert and is the main reason we need such tight mixture control.

PHOTO (COLOR): The ceramic substrate in a typical catalytic converter allows exhaust gas to flow through passages in the block, bringing the gas in contact with the catalyst that's baked onto the surfaces.

PHOTO (COLOR): A schematic showing the ceramic substrate held in place by a metal mesh that cushions vibration. If the substrate overheats and melts, it forms wide open spaces that won't create excess back pressure. The old pellet bed substrates would melt to form a lump that blocks exhaust flow.

PHOTO (COLOR): Jacques Gordon, Technical Editor

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By Jacques Gordon, Technical Editor

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