

Application note

Working Safely with Hydrogen as a Carrier Gas!

by Dr. Konrad Grob, Kantonales Laboratory, Zurich

Broad agreement is that hydrogen is the best carrier gas for capillary GC applications. Nitrogen cannot seriously be considered as a carrier gas option, because diffusion speeds of the solute molecules are roughly four times lower than in hydrogen or helium, rendering the separation process exceedingly slow. Helium is the best alternative if hydrogen cannot be used, but hydrogen enables faster chromatography whenever inlet pressure exceeds roughly 0.7 bar, with a rapidly expanding difference when the required inlet pressure increases. Hydrogen is almost a must for high-temperature work such as triglyceride analysis, and analysis with long columns such as fatty acid methyl ester analysis on 100m columns. Also, hydrogen is available in unlimited amounts (using helium depletes limited natural resources). Hydrogen cannot be used with thermoionic detectors and some mass spectrometers, but the main argument against hydrogen concerns safety because it forms an explosive mixture with air. Can a lab manager take the responsibility for using hydrogen as carrier gas? Yes, if some simple safety measures are taken.

Exploding GC ovens

In the past, there have been many hydrogen explosions in GC ovens. I know of four in Switzerland, the latest one probably being 15 years back. I caused one myself in the seventies during production of glass capillary columns. I prepared about five columns a day using a procedure requiring five heat treatments in a GC oven. I could install a column in hardly more than a second, virtually without turning a screw. I set a high inlet pressure to remove the air and heated the GC at full power to 280°C. One day, a column had enough tension to pull the inlet out of the ferrule. Hydrogen ran into the oven at about 1 bar, without any restriction. The heating filaments were red-hot (2.5 kW, in an old instrument) and ignited

the mixture. The explosion was heard through several labs. The instrument seemed to jump 1-2cm from the bench and lost the dust from its top. Opening the door, I was amazed to see the glass capillary column hanging a bit lower than before, but not being broken. The door did not open as smoothly as before, this being the only reminder of the event.

The other explosion in our lab occurred shortly after an on-column injection for triglyceride analysis. We changed the columns almost daily, and the inlet was installed rapidly, with a soft fitting used many times, tightening by fingers. As the syringe needle did not enter the column inlet easily, my coworker pushed a bit harder than usual. The needle went down and he did the injection. He started the program (with ballistic heating from the injection temperature of 70°C to 250°C) and switched on the recorder. He had just turned his back to the instrument when there was the bang. In fact, he injected into the oven, because the syringe had pushed the column out of the fitting. Again, there was no damage, neither to the instrument, nor to the glass capillary column.

The two other explosions happened in other laboratories, in both instances because it remained unnoticed that the column had been removed from the instrument. Somebody wanted to bake out the column, set high inlet pressure and heated the oven at full power. There was no need for coffee to wake up that morning. The instruments were slightly deformed, but were used for another ten years at least.

4% Hydrogen, 630 °C

We had many large leaks with broken columns, poor connections, and experiments more outrageous than can be described here - and there were no explosions. Beside some good luck, this is due to the fact that explosions of hydrogen are much less likely to occur than explosions of solvent

vapors. A minimum of 4% hydrogen in air is required for an explosion to occur, and the mixture must be heated to about 630°C to be ignited (in contrast to around 0.1% and hardly over 200°C for vapors of many solvents). In fact, all the explosions I know of occurred with old instruments, characterized by high heating power and relatively small filaments, which turned red-hot when heating ballistically. Newer instruments with less heating power and larger filaments hardly reach the temperature for ignition. Also, the 4% concentration is not that easily reached: concluding from the experience of many critical situations, it seems that the two most common risks in practice, breakage of the column or a leaking connection to an injector, hardly ever result in an explosion. All explosions I heard of were the result of unhindered flow of hydrogen from the injector into the oven.

Measures ensuring safety

Hydrogen sensors

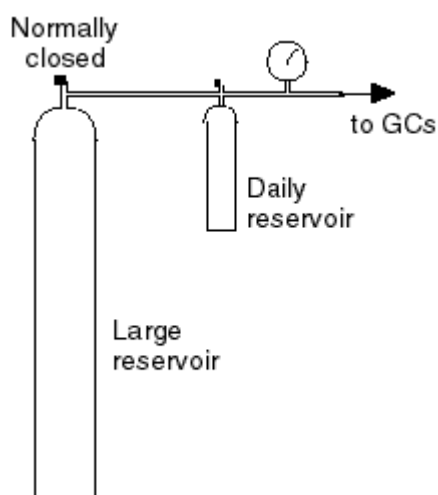
Risks must be taken seriously, even when it seems unlikely that severe damage may occur. Since the early eighties we gradually equipped all of our instruments with hydrogen sensors, a small device available from various sources. Some air is picked from the zone of the oven ventilator and brought to a sensor detecting hydrogen in the concentration range of 0.1 to 1%. When 1% is reached, the gas chromatograph is switched to cooling, which stops the heating and purges the oven with ambient air. Usually a lamp blinks and an alarm signal calls for attention. A luxury version even replaces the hydrogen in the carrier gas line with nitrogen. The sensor also goes off if concentrations of solvent vapors in the laboratory are high, which eliminates a further risk (independently of whether hydrogen or helium is used as carrier gas).

Flow-regulated carrier gas supply

Classical gas chromatographs regulate the carrier gas by pressure. When there is no column, such

systems may deliver many liters of gas per minute into the oven. Hewlett Packard introduced a flow-regulated system, in the worst case limiting the flow into the oven to the rate adjusted for the application, i.e. column plus split plus septum purge flow rate. The maximum flow rate is 500ml/min. Flow regulation strongly reduces risks, but is not considered to be safe. A rough estimation provides some clues. A GC oven has an internal volume of around 40 liters. The explosion limit of 4% is reached when the oven contains 1.6-liter of hydrogen. If the system leaks by 500ml/min, it takes little more than 3 minutes to render the oven atmosphere explosive. If the imposed flow rate is 100ml/min only, however, the critical limit is calculated to be reached in 16 minutes. This assumes a tight oven, which is not realistic; hydrogen diffuses extremely rapidly and the oven atmosphere is exchanged in far less time than 16 minutes. Hence, with a leak of 100ml/min, the hydrogen concentration in the oven cannot reach the explosion limit. Potentially dangerous flow rates exceeding 100ml/min are of interest for split injection with high split ratios. If the high flow rate is turned down 1 minute after the injection, this eliminates this risk and also conserves carrier gas. In splitless injection, the adjusted flow rate will be substantially below 100ml/min anyway. In on-column injection, the flow rate during analysis is far below the critical minimum. It depends on the construction of the injector seal, however, whether the flow rate can be limited to a few milliliters per minute: during injection, a rotating valve leaks at a far higher flow rate, and pressure would collapse when limiting the flow rate to less than about 100ml/min. Hence, flow regulation or a restrictor limiting flow in a pressure-regulated system can exclude a dangerous hydrogen concentration in the oven.

Intermediate storage in small cylinders



Gas supply system ruling out large losses. Gas is consumed from a daily reservoir and the well-observable manometer provides control over the gas consumption

Rather frequently a column is dismantled without switching off the carrier gas supply. Other times a septum leaks to such an extent that the hot carrier gas can burn fingers held many centimeters above the septum. In both these situations, hydrogen may leak into the laboratory at high flow rates. The risk of a laboratory explosion is minimal, however. A small laboratory contains maybe 50,000 liters of air. 4% of hydrogen corresponds to 2000 liters, i.e., to the content of a full 10-liter cylinder at 200 bar pressure. Admittedly, mostly 25- or 50-liter cylinders are used, but since the laboratory atmosphere is exchanged many times per hour, these cylinders would have to be emptied in minutes to reach the explosion limit. Again, hydrogen is far less dangerous than solvents, for many of which 50-liters of vapor is the limit, corresponding to a spill of around 250ml of liquid solvent. And, since the solvent vapors tend to form a "lake" above the floor, the explosion limit is reached locally even more rapidly. A simple safety measure rules out large scale loss of hydrogen and is also a warning of massive leaks: The main reservoir, maybe a 50-liter cylinder, is not directly connected to the laboratory gas

supply, but via a small daily reservoir. The large tank is closed (except when almost empty). The gas is consumed from a 3- to 10-liter cylinder, adjusted to the daily consumption. A 3-liter cylinder filled up to 50 bar contains 150 liters of hydrogen. If, for instance, three gas chromatographs consume 100ml/min each (25ml/min for the FID), the cylinder must be refilled every 25 hours, which suits when these instruments work day and night. If filled to 20 bar only, it would contain an amount well fitting the consumption of a working day. A manometer or an electronic readout is positioned such that everybody will see it. If the daily reservoir must be refilled on the same day, this is a warning and a leak will be detected long before the large reservoir is emptied. The manometer can be equipped with an alarm indicating low pressure. In Switzerland, this is a standard installation found in many laboratories for more than 20 years.

Hydrogen generators

Hydrogen generators are an alternative to the small daily reservoir. They deliver the gas at limited flow rates and totally avoid the necessity of storing gas. If split injection must be possible at high split flow rate, however, rather large generators and/or one for every few instruments are needed.

Conclusion

I understand the dilemma of the laboratory manager: he or she may recognize that hydrogen is preferable and cheaper than helium, but does not want to take risks. Can these risks be managed? Hydrogen sensors rule out explosions in the oven, and daily reservoirs or hydrogen generators eliminate risks in the laboratory (as well as costs caused by large losses). Checking tightness of the gas plumbing every 6-12 months is also advisable whether hydrogen or helium is used.