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APPLICATION NOTE

Thermo Scientific™ Prima PRO Process Mass Spectrometer

Improving process control and efficiency in Ammonia production

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Keywords
- Steam to carbon ratio
- Air requirement
- Methane slippage
- Shift reaction
- H/N ratio
- Rapid multi-stream sampler
- Magnetic sector analyzer

Introduction
Ammonia is one of the most important industrial chemicals in the world; global production was 140 million tonnes in 2016, with global capacity expected to increase by 10% during the next 4 years[1]. Around 80% of ammonia is processed into downstream fertilizer products, including urea, ammonium nitrates, ammonium sulfate and ammonium phosphates. It is also used to produce explosives, synthetic fibers and plastics, including acrylics, polyurethanes and nylon. With the exception of China, where much of the ammonia is produced from coal gasification, most of the world's ammonia is produced from natural gas[2].The key raw material for the ammonia production process is therefore natural gas. Raw material prices are obviously heavily affected by demand for power generation and heating fuels; in the same way, downstream fertilizer product prices are affected by political, economic and environmental factors. This puts great pressure on the ammonia production unit to maximize efficiency.

The Ammonia process
The manufacture of ammonia can be simply described by the classic Haber process formula:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

However there are a number of process steps required to produce the two reactants from the raw materials of fuel, steam and air. All these steps take place in the gas phase and require fast, accurate gas analysis if the process is to be optimized.

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Figure 1 shows a simplified schematic of a typical ammonia plant based on natural gas feedstock, with typical sample points identified.

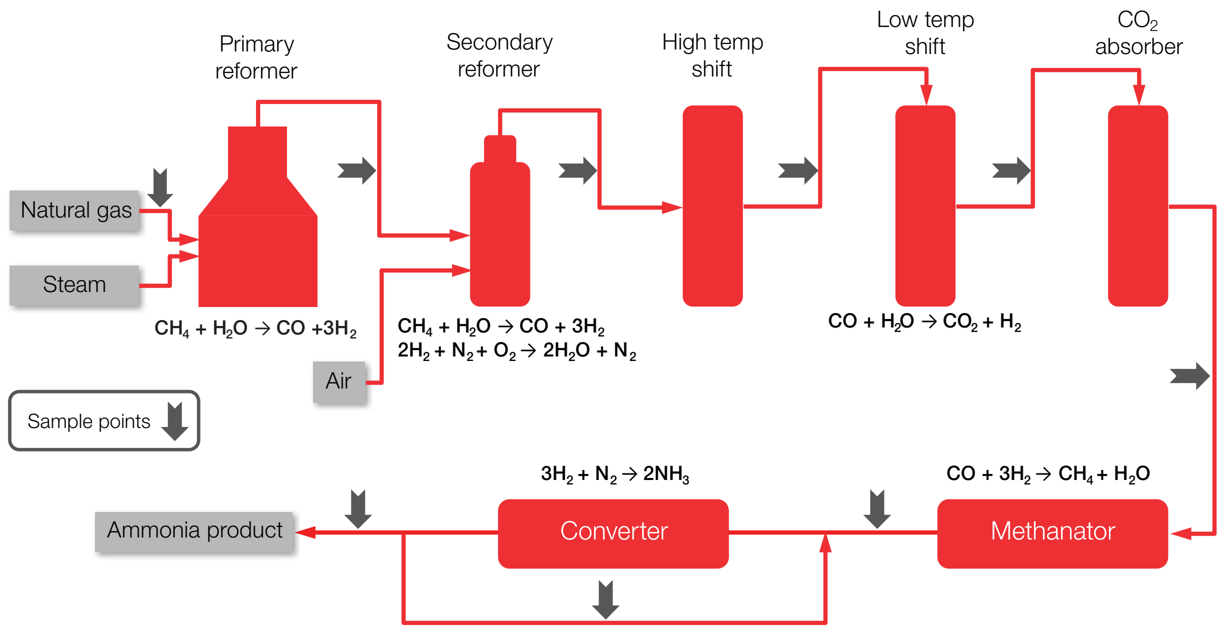

Figure 1 : Typical ammonia process schematic

Process analytical requirements

The various ammonia process streams contain a wide range of organic and inorganic compounds

- **Organics: C_1 to C_5 hydrocarbons**
- **Inorganics: N_2, H_2, NH_3, CO, CO_2, O_2, Ar, H_2S**

Concentrations range from tens of percent down to parts per million. In theory a set of discrete analyzers could be used to measure some of the require components, but installation and maintenance costs will be extremely high and vital analysis information will be missing. Alternatively process GC could be used, but long analysis cycle times and frequent calibration and maintenance intervals limit the usefulness of the technique. The only practical multi-point, multi-component solution is process mass spectrometry. This can provide fast, accurate and reliable process information that can be used as part of a dynamic process control model.

Advantages of mass spectrometry

Mass spectrometers offer analysis times measured in seconds rather than minutes and the ability to measure both inorganic and organic species over a wide dynamic range. One mass spectrometer can therefore monitor all the sample point on the ammonia process, from feedstock to final product.

Key control parameters

Steam to carbon ratio

Steam and natural gas (or another source of hydrocarbon) are reacted together in the primary reformer to form hydrogen and carbon monoxide:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

Some of the carbon monoxide will react with the steam to form more hydrogen:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The steam to carbon gas ratio needs tight control, otherwise energy is wasted as excess steam is produced unnecessarily. Excess methane requires more energy for compression and causes inefficient catalyst activity.

Air requirement

As well as being the process's source of hydrocarbon, natural gas is also used as fuel. The physical properties of the fuel gas must be measured accurately, so the air requirement for combustion control optimizes the production unit's energy consumption.

Methane slippage

Only 30-40% of the hydrocarbon is converted in the primary reformer. The exhaust is therefore fed into a secondary reformer where the conversion to carbon monoxide and hydrogen continues. Air is introduced at this stage to provide nitrogen, and combustion takes place at around 1250°C.

It is important to minimize the amount of unreacted methane, or methane slippage, out of the secondary reformer. Methane builds up in the ammonia converter loop; this process takes place at high pressure and methane needs more compression energy, which reduces ammonia yield.

Shift reaction

It is important to remove all carbon monoxide from the process before it reaches the ammonia converter, as it poisons the catalyst. This is done by 'shifting' carbon monoxide to carbon dioxide, then absorbing the carbon dioxide. The shift takes place in two steps, the high- and low- temperature shifts. It is important to remove carbon monoxide as it can shift back to methane, a highly exothermic reaction that can damage the next process stage, the methanator.

H/N ratio

The methanator is designed to remove any residual carbon monoxide and carbon dioxide. The output from the methanator is syn-gas and ideally should be made up of 75% hydrogen and 25% nitrogen; in practice there will also be some residual methane and argon from air. The production of ammonia takes place over an iron oxide catalyst in the converter; it is vital to keep the ratio of hydrogen and nitrogen as close as possible to the stoichiometric ratio of 3 to 1.

Analyzer requirements

The ammonia process application presents a series of challenges to the Process MS. The Prima PRO from Thermo Fisher Scientific has been designed to meet and beat these challenges.

Rapid multistream sampling

If the MS is to monitor all process streams then a fast, reliable means of switching between streams is required. Solenoid valve manifolds have too much dead volume and rotary valves suffer from poor reliability so we developed the unique RMS Rapid Multistream Sampler (RMS). It offers an unmatched combination of sampling speed and reliability and allows sample selection from 1 of 32 or 1 of 64 streams. Stream settling times are application dependent and completely user configurable. The RMS includes digital sample flow recording for every selected stream. This can be used to trigger an alarm if the sample flow drops, for example if a filter in the sample conditioning system becomes blocked.

The RMS can be heated to 120°C and the position of the stream selector is optically encoded for reliable, software controlled stream selection. Temperature and position control signals are communicated via Prima PRO's internal network.

The RMS is shown in schematic form in figure 2. It has a three year warranty as standard; no other multistream sampling device offers the same level of guaranteed reliability.

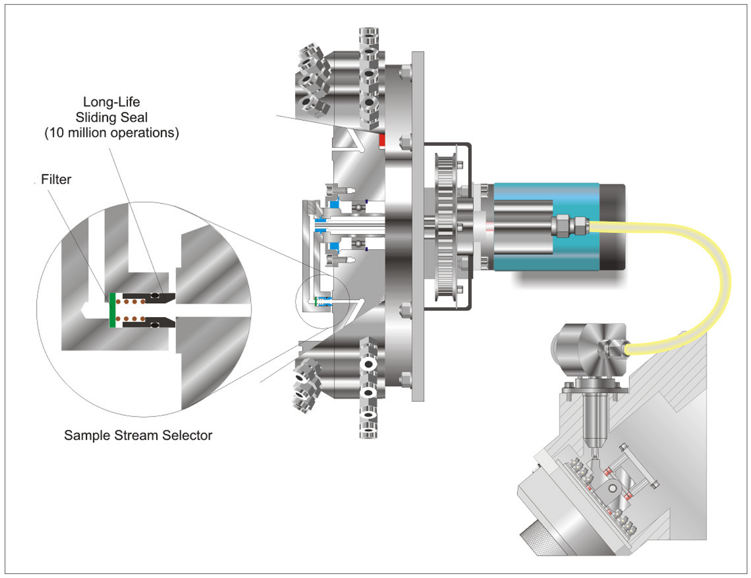

Figure 2 Rapid Multistream Sampler

Precision of analysis

The MS is required to monitor a wide range of component concentrations; if these data are to be used as part of a dynamic plant control strategy they must be reliable and available.

At the heart of the Prima PRO is a magnetic sector analyzer which offers unrivalled precision and accuracy compared with other mass spectrometers. Thermo Fisher Scientific manufactures both quadrupole and magnetic sector mass spectrometers; over thirty years of industrial experience have shown the magnetic sector based analyzer offers the best performance for industrial on line gas analysis.

Key advantages of magnetic sector analyzers include improved precision, accuracy, long intervals between calibrations and resistance to contamination. Typically, analytical precision is between 2 and 10 times better than a quadrupole analyzer, depending on the gases analyzed and complexity of the mixture.

Neutral gas atoms and molecules are first converted into positively charged ions in the Prima PRO ion source. This is an enclosed type for high sensitivity, minimum background interference and maximum contamination resistance. It is a high-energy (1000 eV) analyzer that offers extremely rugged performance in the presence of gases and vapors that have the potential for contaminating the internal vacuum components. Prima PRO has a proven track record of monitoring high percent level concentrations of organic compounds without experiencing drift or contamination.

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Table 1 Typical Prima PRO stream performance specifications

Stream #	1		2		3		4		5		6	
Component	Natural gas stream (Primary Reformer Feed)		Primary reformer effluent		Secondary reformer effluent		High temperature shift reactor outlet		Low temperature shift reactor outlet		CO_2 absorber outlet	
	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol
H_2	0 ~ 1	0.002	65 ~ 70	0.03	55 ~ 65	0.03	55 ~ 70	0.03	70 ~ 75	0.03	65 ~ 83	0.03
CH_4	80 ~ 95	0.02	9 ~ 13	0.01	0.5 ~ 2	0.002	0.1 ~ 0.5	0.001	0.1 ~ 0.5	0.001	0.1 ~ 0.5	0.001
NH_3												
CO			9 ~ 10	0.03	10 ~ 14	0.03	1 ~ 3	0.03	0.1 ~ 0.5	0.02	0.1 ~ 0.5	0.02
N_2	2 ~ 5	0.01	0.1 ~ 3	0.02	23 ~ 24	0.02	15 ~ 21	0.02	9 ~ 15.0	0.01	15 ~ 20	0.01
C_2H_6	1 ~ 5	0.005										
Ar			0.1 ~ 0.5	0.001	0.1 ~ 0.5	0.001	0.1 ~ 0.5	0.001	0.1 ~ 0.5	0.001	0.1 ~ 0.5	0.001
CO_2	1 ~ 3	0.005	9 ~ 12	0.01	8 ~ 10	0.01	12 ~ 17	0.01	9 ~ 12	0.01	0.1 ~ 0.5	0.001
C_3H_8	1 ~ 3	0.005										
i-C_4H_{10}	0 ~ 1	0.005										
n-C_4H_{10}	0 ~ 1	0.005										
i-C_5H_{12}	0 ~ 0.5	0.005										
n-C_5H_{12}	0 ~ 0.5	0.005										
C_6H_{14}	0 ~ 0.5	0.005										

Stream #	7		8		9		10		11	
Component	Synthesis gas		Convertor inlet		Convertor outlet stream		High pressure purge		H2 recovery	
	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol	Typical comp % mol	Precision (Std Dev) % mol
H_2	65 ~ 75	0.02	62 ~ 70	0.02	55 ~ 60	0.02	60 ~ 62	0.02	90 ~ 100	0.01
He	0.5 ~ 1	0.002	0.5 ~ 1	0.002					0 ~ 5	0.003
CH_4	3 ~ 10	0.01	5 ~ 10	0.01	5 ~ 10	0.01	1 ~ 12	0.01	1 ~ 5	0.002
NH_3			1 ~ 3	0.002	10 ~ 15	0.01	1 ~ 5	0.005		
CO										
N_2	20 ~ 26	0.01	20 ~ 26	0.01	15 ~ 22	0.01	20 ~ 25	0.01	2 ~ 5	0.002
C_2H_6										
Ar	0.1 ~ 5	0.002	1 ~ 5	0.002	1 ~ 5	0.002	2 ~ 5	0.002	0.5 ~ 3	0.002

A set of typical performance specification for the Prima PRO on eleven ammonia process streams is shown in Table 1. This shows the 8 hour analysis precision (single standard deviation) based on an analysis time of 20 seconds including stream switching time. Thermo Scientific GasWorks software permits analysis optimization on a per-stream basis so we can select the most appropriate speed versus precision setting depending on process control requirements. Similarly we can select the most efficient peak measurements for each stream and the most appropriate display units (% or ppm).

We issue a guaranteed performance specification for the Prima PRO based on an individual customer's specific stream details. This performance will be demonstrated during start-up by one of our trained engineers, included as standard in the price of the Prima PRO.

Analysis of low level carbon monoxide

The gas exiting the Low Temperature Shift (LTS) reactor contains very low levels of carbon monoxide, typically between 0.1% and 0.5%. The analysis of trace levels of carbon monoxide in the presence of percentage levels of carbon dioxide and nitrogen presents a problem to all process mass spectrometers because their spectra overlap with one another. In all the other process streams containing these three species, the carbon monoxide levels are high enough to allow the use of fragment peaks. In the LTS reactor outlet the large amount of spectral overlap means the CO measurement precision is reduced. Prima PRO's lower detection limit for carbon monoxide in this stream is 0.3 % mol, with a standard deviation of 0.02%. We therefore recommend analysis of CO in the LTS by a dedicated Non-Dispersive Infra-Red analyzer. It is easy to integrate the NDIR CO analysis with the MS data; we simply fit a connector to the RMS which selects the sample for the MS to analyze and, at the same time, diverts a fast loop to the external NDIR analyzer. And of course the Prima PRO can be used to provide a backup alarm for CO break-through.

Using MS data to control the process

The unique combination of magnetic sector stability, fast multistream switching and GasWorks quantitative software ensures the process data produced by the Prima PRO is accurate and reliable. A range of industry standard communication protocols can transfer this data to process control systems to optimize the ammonia process.

Steam to carbon ratio

Prima PRO has been independently evaluated by EffecTech UK, an independent specialist company providing accredited calibration and testing services to the energy and power industries for gas quality, flow and total energy metering. It is accredited to internationally recognised ISO/IEC 17025:2005 standards; this specifies the general requirements for the competence to carry out tests and/or calibrations, including sampling.

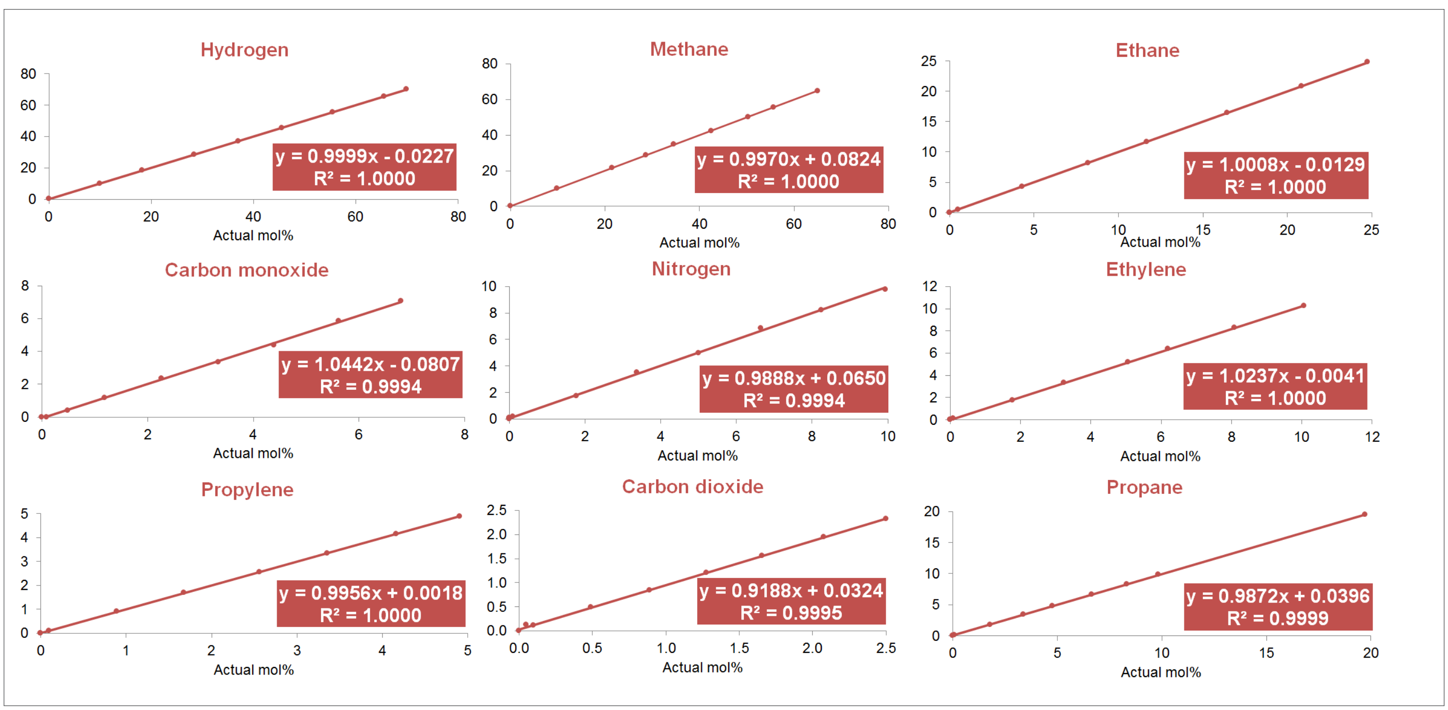

Figure 3 Prima PRO linearity data

Prima PRO was calibrated for sensitivity using just one gas mixture, and then tested with a set of nine reference gases covering a wide range of compositions. Figure 3 shows the linearity plots generated by EffecTech. They demonstrate significantly better linearity than that achieved by a thermal conductivity detector fitted to a gas chromatograph, and prove that Prima PRO is capable of generating accurate, reliable composition data from complex gas mixtures.

Prima PRO's GasWorks software supports an unlimited number of Derived Values, on-line calculations that can be included as part of any analysis method. So GasWorks can calculate the steam to carbon ratio—it just needs two analog inputs, one for steam flow in weight per unit time, and the other for natural gas flow, also in weight per unit time. Alternatively the MS can simply transfer the composition data to the DCS using one of its industry standard communication protocols.

Inerts in recycled gas

Just 30% of syn-gas is converted to ammonia as it passes through the converter, so a recycle stream returns the outlet stream for re-processing. It is important to monitor inert gases such as argon and helium in the recycle stream, as these gases take no part in the reaction and their concentrations gradually build up as the stream is continuously recycled. Clearly, the more frequently these points can be monitored, the better the control of this final stage of the process.

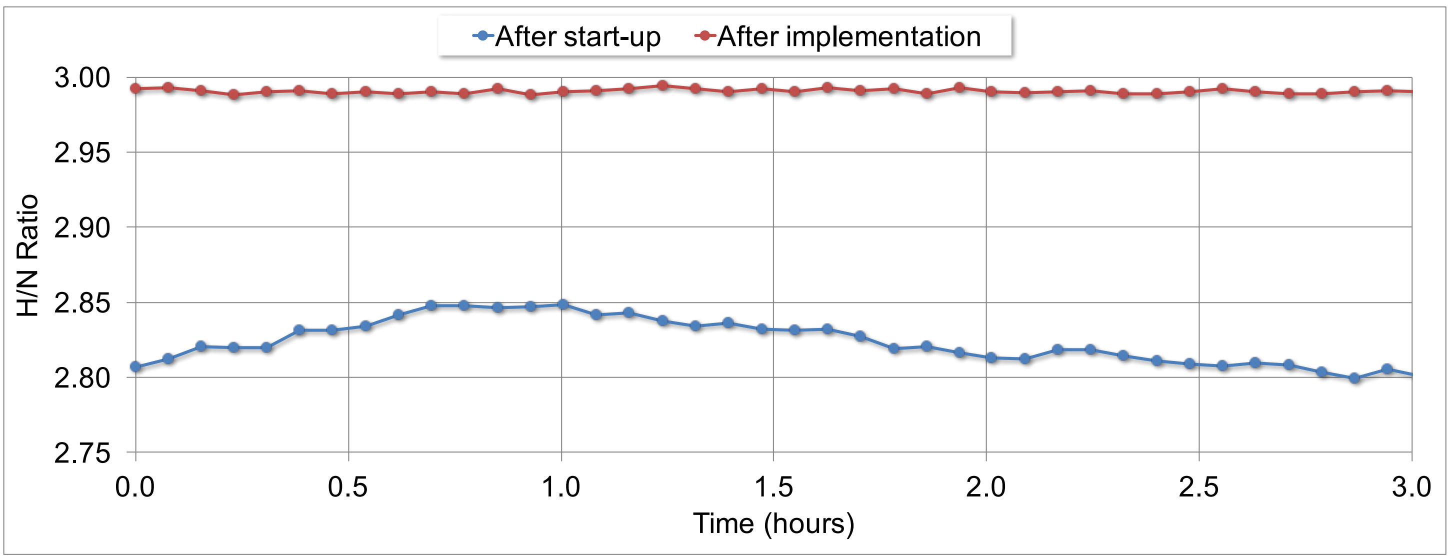

Figure 4 Improving H/N ratio with Prima PRO

Improving H/N ratio

Prima PRO MS measures the H/N ratio with a relative precision of 0.05%, which is a precision of 0.0015 on a ratio of 3.1 Example process H/N ratio is shown in Figure 4. The blue trend is the ratio immediately after the MS was installed; the red trend is the ratio after implementing process control improvements, based on data from the MS. The standard deviations achieved during these two runs are shown in Table 2.

Summary

Prima PRO offers the best available online measurement precision and stability for ammonia process monitoring and control. Its fault tolerant design combined with extended intervals between maintenance and simplified maintenance procedures ensures maximum availability. The standard service kit shipped with every Prima PRO shown in Figure 5 provides users with all the parts and tools to carry out the simple maintenance procedures required to maintain the analyzer; our confidence in the Prima PRO's reliability is reflected in the industry-best 3-year parts and labor warranty.

Table 2 Examples of H/N ratio before and after process improvements

	After start-up	After implementation
Average H/N ratio	2.824	2.991
Standard deviation	0.015	0.001
Relative standard deviation	0.5%	0.05%

Prima PRO benefits

- Optimize gas mixing & burner control in reformer
- Optimize Steam/carbon ratio
- Monitor H_2S in natural gas
- Optimize H/N ratio: 0.05% RSD
- Optimize methane slippage ± 20 ppm accuracy
- Monitor inert gas build-up in synthesis loop
- Monitor catalyst activity to schedule plant outages

Reference

1. U.S. Geological Survey, Mineral Commodity Summaries, January 2017.
2. Chemical Economics Handbook – Ammonia, July 2017.

Figure 5 Prima PRO service kit

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