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Air Separation Process Analysis Using the VG Prima δB

Key Words

- Mass Spectrometry
- Air Separation
- Argon Plant
- Column Profiling
- Pure Oxygen
- Pure Nitrogen
- Pure Argon

Thermo Industrial Solutions Note

Introduction

Air separation plants are used to generate pure oxygen, pure argon, and pure nitrogen for use in steel, metallurgical, petrochemical, and semiconductor processes. Optimization of the plant and verification of product quality require fast, accurate analysis, and process mass spectrometry is ideally suited for this purpose.

Air Separation Unit

Large scale Air Separation Units (ASUs) employ a four-stage cryogenic air separation process: Compression, Prepurification, Liquefaction and Distillation. In the first stage, ambient air is compressed and chilled. The second stage consists of an air prepurification system that uses dual molecular sieve beds (one in use while one is being regenerated) to remove CO_2, H_2O, N_2O and hydrocarbons from the feed air. The third stage in the process comprises a heat exchanger and an expansion turbine. A high-pressure gas stream is expanded across the turbine, producing a cold gas stream that is used in the heat exchanger, to condense the feed air to the liquid. The fourth stage consists of distillation column which separates the liquefied air into pure nitrogen, pure oxygen and pure argon.

In some plants, argon from the ASU is reacted with 2-7% hydrogen over a palladium catalyst to convert any residual oxygen to water. This feed must contain less than 5% O_2 otherwise the purifier catalyst may overheat. The argon product contain <3 ppm O_2 and <10 ppm N_2.

From this brief description, it is clear that there are a number of different applications for gas analysis in the ASU process. This note is concerned with column profiling using the analysis of gas compositions at various points in the distillation column in order to optimize plant operation.

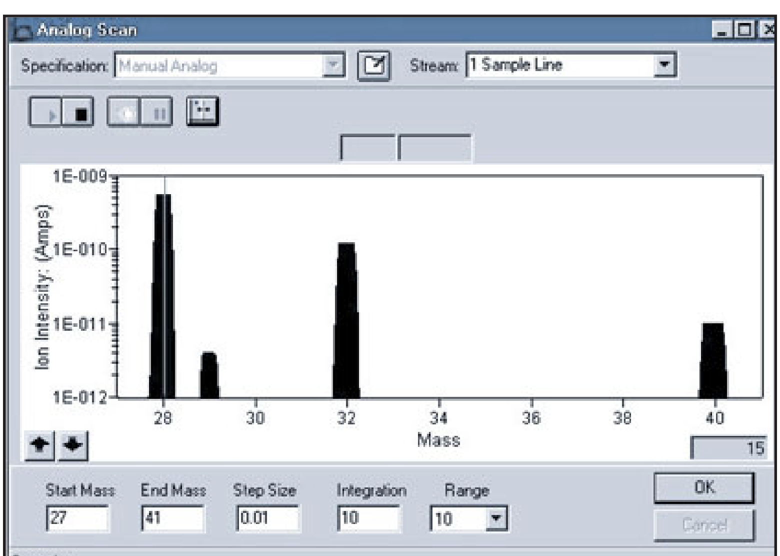

figure 1 – MS peaks at masses 28 and 29 (N_2), 32 (O_2) and 40 (Ar) obtained with VG Prima δB magnetic mass analyzer

Benefits of Process MS

Process MS is ideally suited to replace the large number of discrete analyzers that are typical in ASU plants.

Recent advances in the design of both hardware and software mean that process MS compares favorably with multiple discrete analyzers in terms of reliability, cost of ownership, and ease of use. Furthermore, because of its greater speed and precision, it is able to offer column profiling, which can be utilized to improve control and yield.

The analysis of the three components of interest (N_2, O_2, and Ar) in widely varying proportions is difficult to perform by any technique other than MS. Although paramagnetic analyzers and zirconia cell analyzers are available for O_2 analysis, N_2 and Ar are effectively 'invisible' to techniques apart from GC and MS. The separation of Ar and O_2 is very simple, involving the monitoring of their three respective ions signals at the three distinct masses 28, 32, and 40 (see *figure 1*).

The analysis is quick (typically three seconds), very precise, linear, and stable (see *figure 3*).

Measurement	Mean Molar % over 24 h	Std dev Molar % over 24 h	% Rel Std dev over 24 h
O_2 (3 sec analysis)	20.94905	0.00268	0.01281
O_2 (30 sec analysis)	20.94904	0.00134	0.00642

figure 2 – 24 hour precision data for VG Prima δB for oxygen analysis

VG Prima δB Performance

The VG Prima δB is a magnetic sector process MS. The system has been designed for optimum performance and uses a magnetic sector mass analyzer in order that the ion signals generate uniform intensity over a wide proportion of the peak width.

The characteristic "flat topped" peak is shown in *figure 1*. The ion beam is created at high energy, 1000 eV, so the influence of space charge or insulating surfaces is minimized. Also, the extraction from the ionization region is faster, resulting in reduced ion-molecule interaction and improved linearity. Long term reproducibility data to 0.01% relative have been achieved.

As an example, the data in *figure 3* shows the analysis of oxygen over 24 hours by VG Prima δB. The graph shows the stability of the oxygen concentration data using the results acquired from 3 second analysis of the three gases N_2, O_2, and Ar in air and also the data acquired by longer analysis, 30 seconds. The unit was calibrated with O_2 at 20.95% prior to the test run. The statistical summary of the oxygen data over 24 hours is shown in figure 2. The analysis is very stable (see *figure 3*), with a reproductability of ±0.01% even for a very short analysis time (3 seconds) for the three gases N_2, O_2, and Ar. Using an analysis time of 10 times longer gives a factor of 2 improvements in stability. The fact that the improvement is not as good as the square root of 10 (3.3) indicates that the noise is not entirely Gaussian in distribution and cannot be totally eliminated by filtering. There is a finite, very small amount

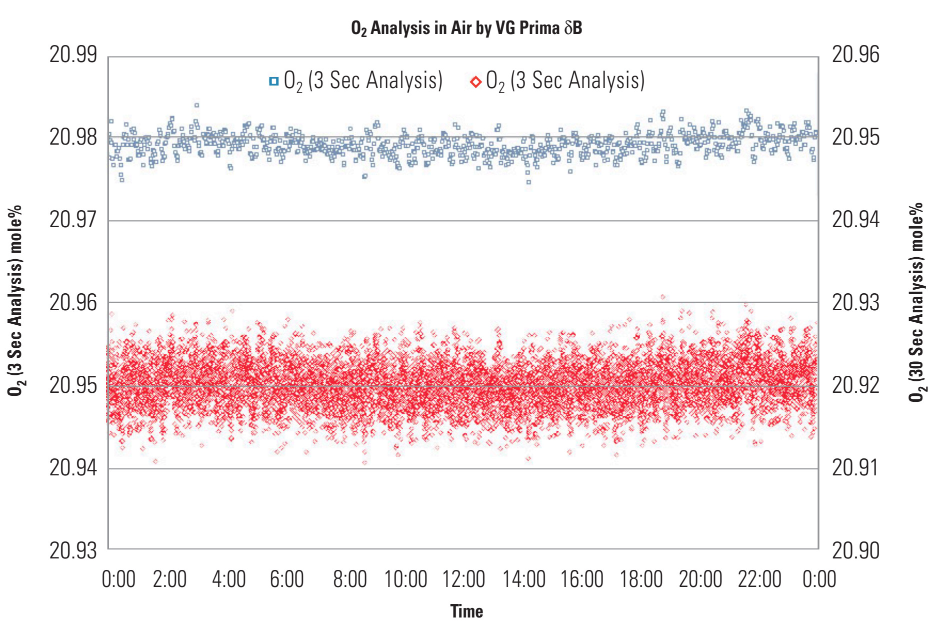

figure 3 – Oxygen precision data obtained over 24 hours with VG Prima δB

Gravimetrically prepared sample		VG Prima dB analysis		
		Actual conc.Molar %	Mean conc.Molar %	Std dev absoluteMolar%
1	N_2	—	—	—
	Ar	0.0100	0.0103	0.0002
	O_2	balance	99.9897	0.0002
2	N_2	—	—	—
	Ar	balance	99.9883	0.0004
	O_2	0.0100	0.0117	0.0003
3	N_2	balance	60.0045	0.0184
	Ar	30.0000	30.0000	0.0140
	O_2	10.0000	9.9955	0.0050
4	N_2	balance	80.0109	0.0043
	Ar	19.0000	18.9876	0.0043
	O_2	1.0000	1.0014	0.0002
5	N_2	balance	99.4925	0.0004
	Ar	0.5020	0.5048	0.0002
	O_2	0.0050	0.0027	0.0002

figure 4 – Test of linearity of VG Prima ∂B for ASU application

of drift-like variation. It is interesting to note that the exceedingly high precision data generated by the VG Prima δB is comparable to that observed on a multi-Faraday collector magnetic sector MS (e.g. for isotope analysis) where time dependent effects are eliminated.

The VG Prima δB is a scanning single Faraday collector instrument which has benefited from advances in improved design of electronic devices for ion production and detection. In particular, the feedback control circuit for the rate of electron impact ionization has been considerably refined.

Before the VG Prima δB was implemented on an ASU, it was evaluated in terms of linearity.

The system was first calibrated using 99.999% N_2, 99.999% Ar, and a 60.0% N_2/30 Ar/10% O_2 mixture. The instrument was then subjected to tests with various gas mixtures prepared by gravimetric means. The results are shown in *figure 4*. The results indicated very high linearity. For example O_2 was calibrated at 10%, but when tested at 1.0000%, the analysis gave 1.0014%, which indicates linearity of better than 0.2% relative over a decade change in concentration.

The errors were in fact comparable to the possible errors in the preparation of the mixtures.

VG Prima δB Benefits

Multi-component analysis at various sample points on an ASU distillation column is being utilized to improve control of the process. In particular, column composition profiling has been used to provide gas density information for optimum valve control.

Additionally, it has enabled an ASU plant to increase crude argon production by maximizing the argon peak in the feed column without generating high levels of nitrogen (> 200 ppm) in the stream.

High concentrations of nitrogen would cause a process upset.

By profiling the feed column, the feed flow into the crude argon column can be maximized while working within the nitrogen concentration constraints and still operate under safe plant conditions.

The principle is illustrated in *figure 5*, where point A represents a typical running state without process MS and point B shows what is possible with process MS. The case for ASU control using process MS

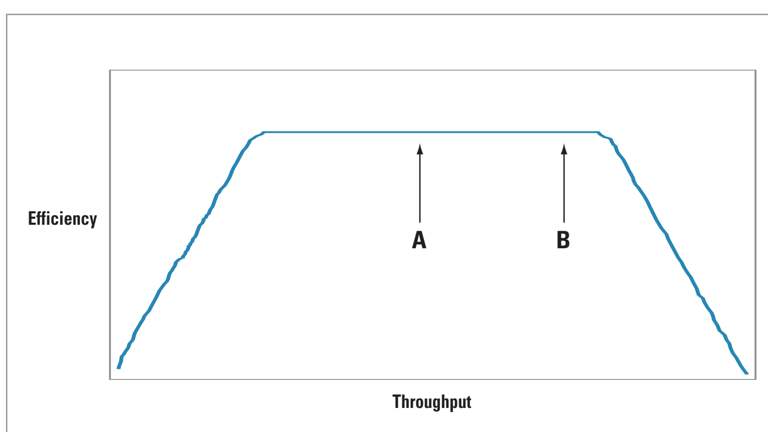

figure 5 – ASU plant operation, showing normal running point A, with VG Prima δB making running at point B possible

is particularly strong, when one considers the cost of such an instrument is typically less than 1% of the annual sales of an ASU plant.

Summary

The following conclusions can be drawn concerning the use of the VG Prima δB for air separation plants.

- VG Prima δB can analyze nitrogen, oxygen and argon with very high reproductability and linearity and at high speed.
- These measurements can be used for ASU column profiling and lead to enhanced throughput.

VG Prima δB from Thermo Electron Corporation is a magnetic sector Process MS, combining high speed with excellent stability. The ultra stable magnetic sector analyzer lends itself ideally to this demanding application.

It benefits from being housed in a rugged, industry standard enclosure and has the advantages of the unique Rapid Multi Stream inlet system, GasWorks software for flexibility, ease of use, and a host of plant interfacing technologies. The standard analytical performance specifications for the ASU application is shown in *figure 6*. For other components and ranges please consult the factory.

Component	Sample gas % Molarconcentration	Precision[1] % absolute
Nitrogen	33.33	0.01
Oxygen	33.33	0.01
Argon	33.33	0.01

[1.] Precision is the standard deviation observed over 24 hours.

Analysis time is 5 seconds for measurements of N_2, O_2, and Ar, together with 10 seconds flushing time, giving a total analysis time per stream of 15 seconds.

Typical recalibration interval is one month.

figure 6 – Standard VG Prima δB analytical performance specifications for the ASU application

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