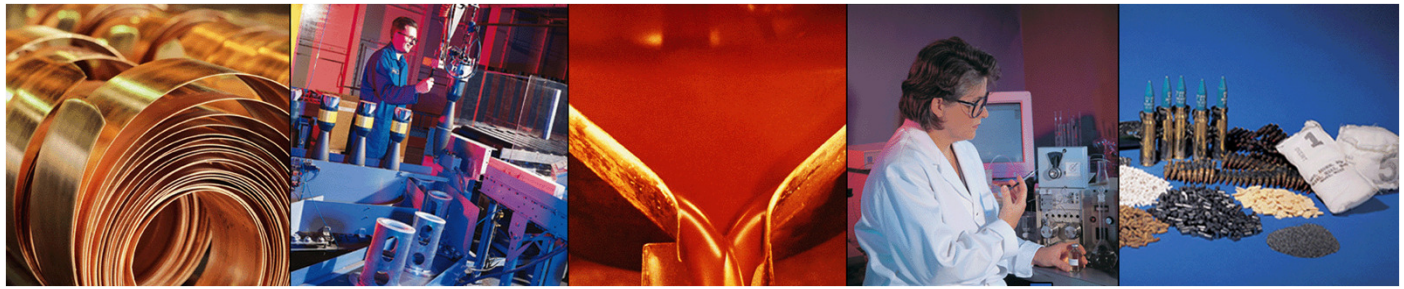
GENERAL DYNAMICS
Ordnance and Tactical Systems–Canada Valleyfield



Nitrocellulose nitrating acids: expressing the content of the various constituents, review of the analytical methods, estimating the analytical precision requirements and establishing specification limits

5th International Nitrocellulose Symposium
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Prepared by Mario Paquet

NC nitrating acid: Establishing tolerance

The requirements for control of the nitrating acid is an important part of nitration process control. Establishing a set of requirements is complicated by the large variations in response from the various mixture of nitrating acid.

This can be estimated from the graphs of composition acid mixture relative to nitrogen content in NC; the two most often used are from Miles and from Brissaud:

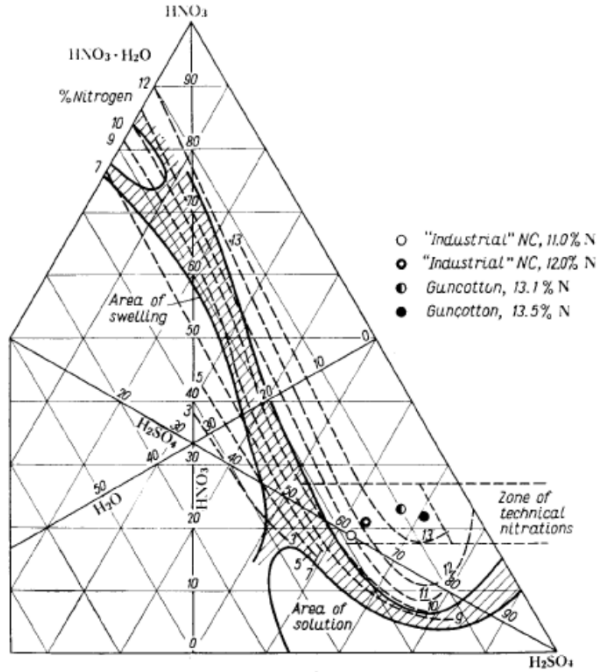


FIG. 123. Sapozhnikov diagram modified by Miles and Milbourn [20]. Composition of acid mixtures in weight %.

Cellulose Nitrate: F.D.Miles, Interscience publishers NY, 1955, p. 66

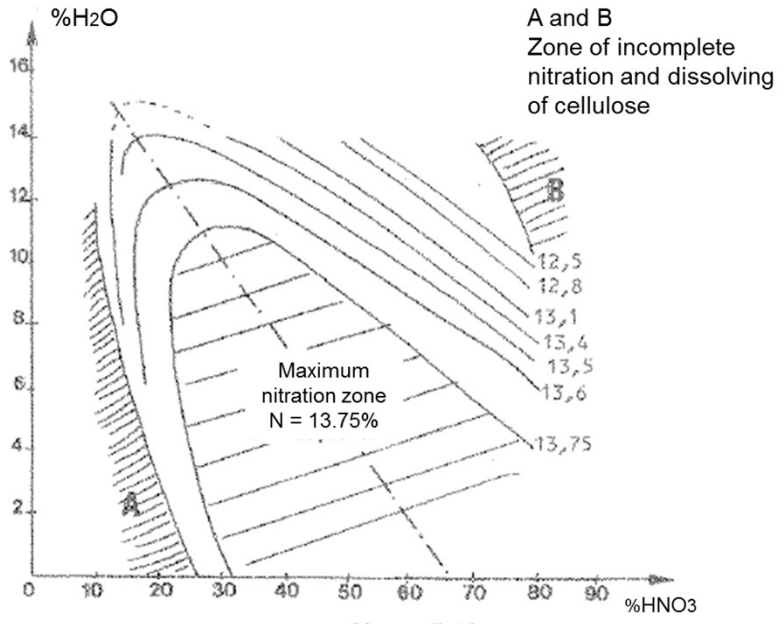
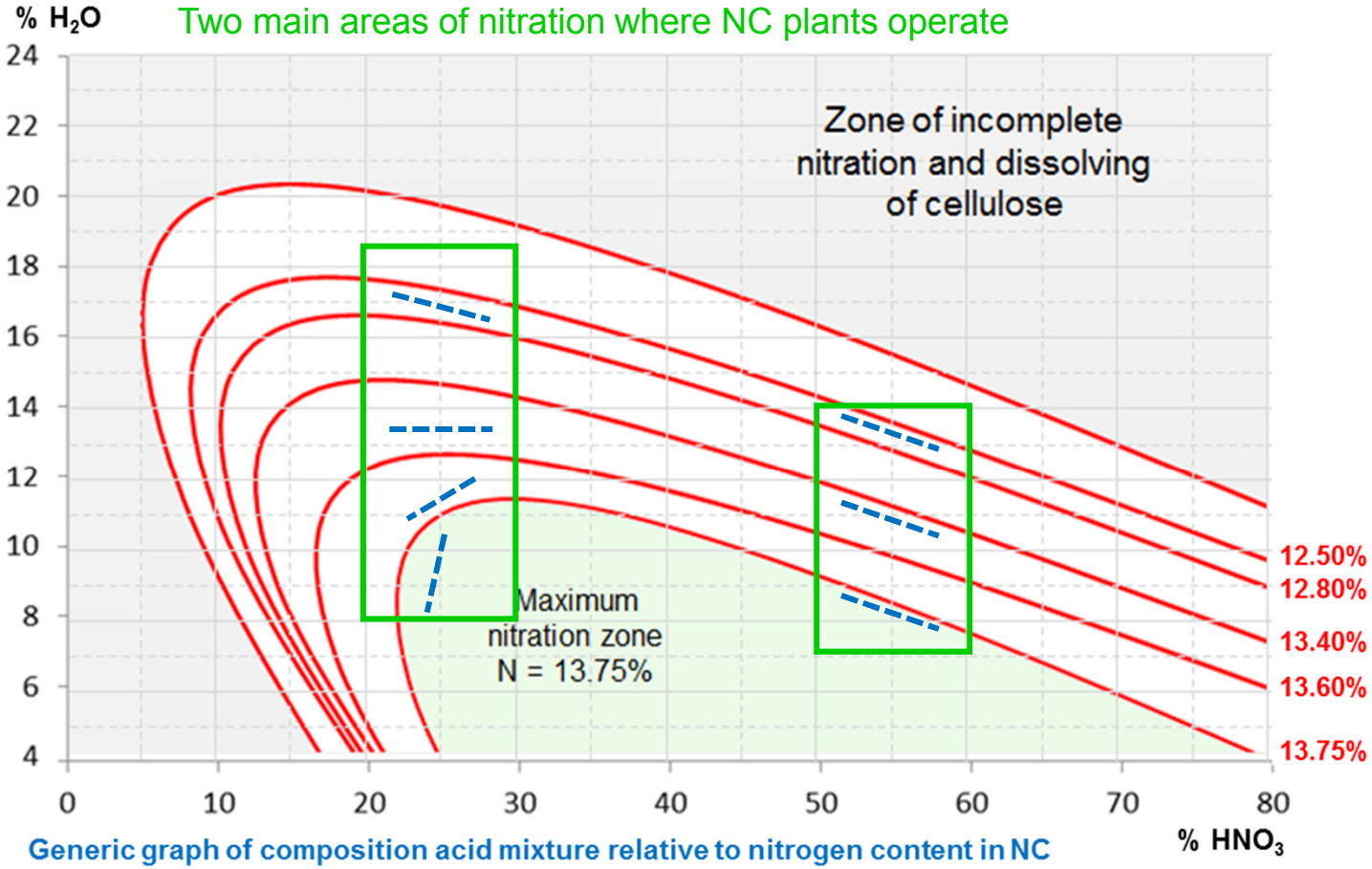


Fig 1.13 Average nitrogen content of NC at equilibrium in a Nitric/Sulfuric nitration acid mix (ref: Brissaud)

Poudres, Propergol and explosives, Volume 2: J.Quinchon and J.Tranchant, 1984, p.25

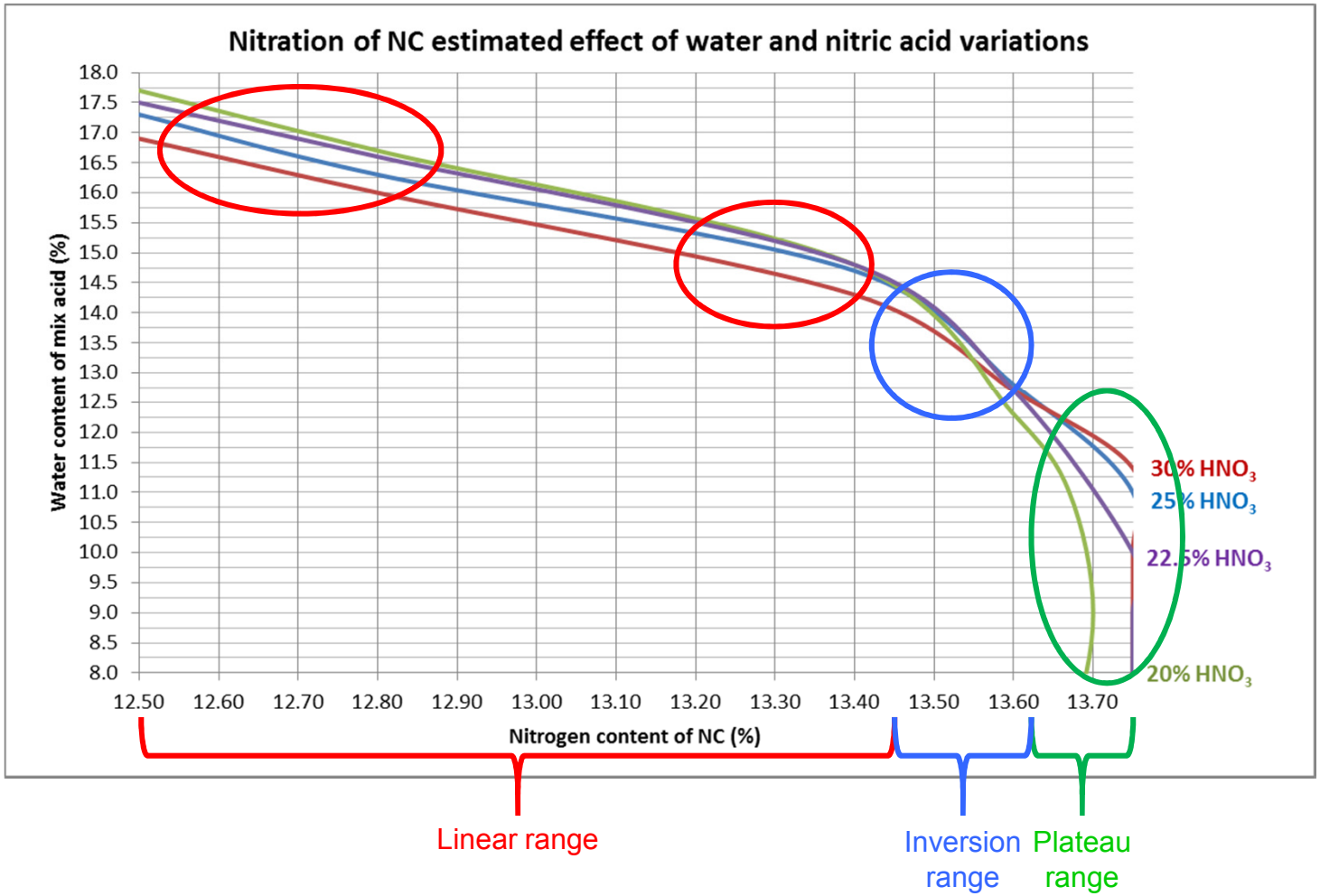
NC nitrating acid: Establishing tolerance



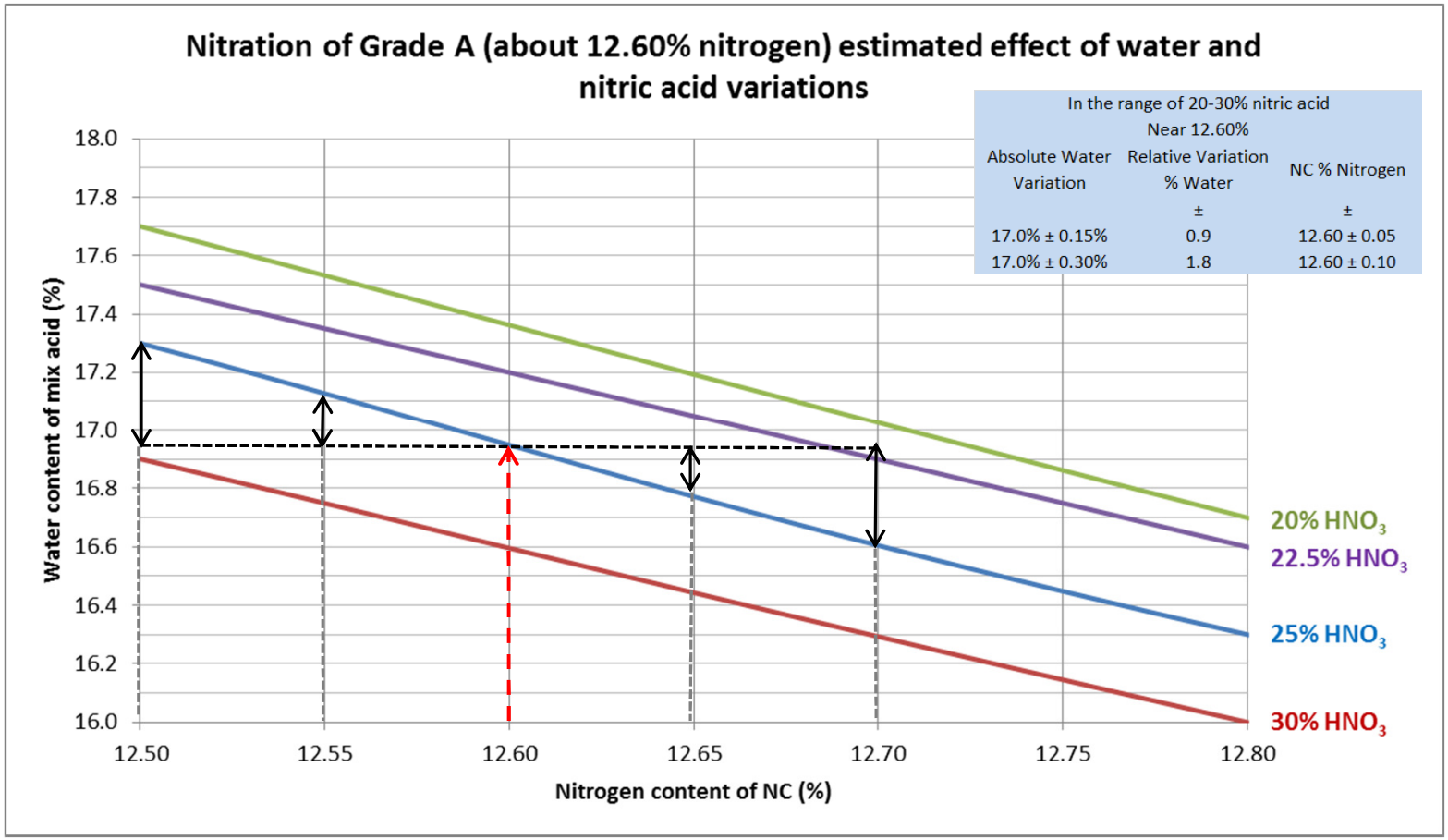
Generic graph of composition acid mixture relative to nitrogen content in NC

Average nitrogen content at equilibrium in Nitric/Sulfuric/Water nitration acid mix
(Data from Miles and Brissaud)

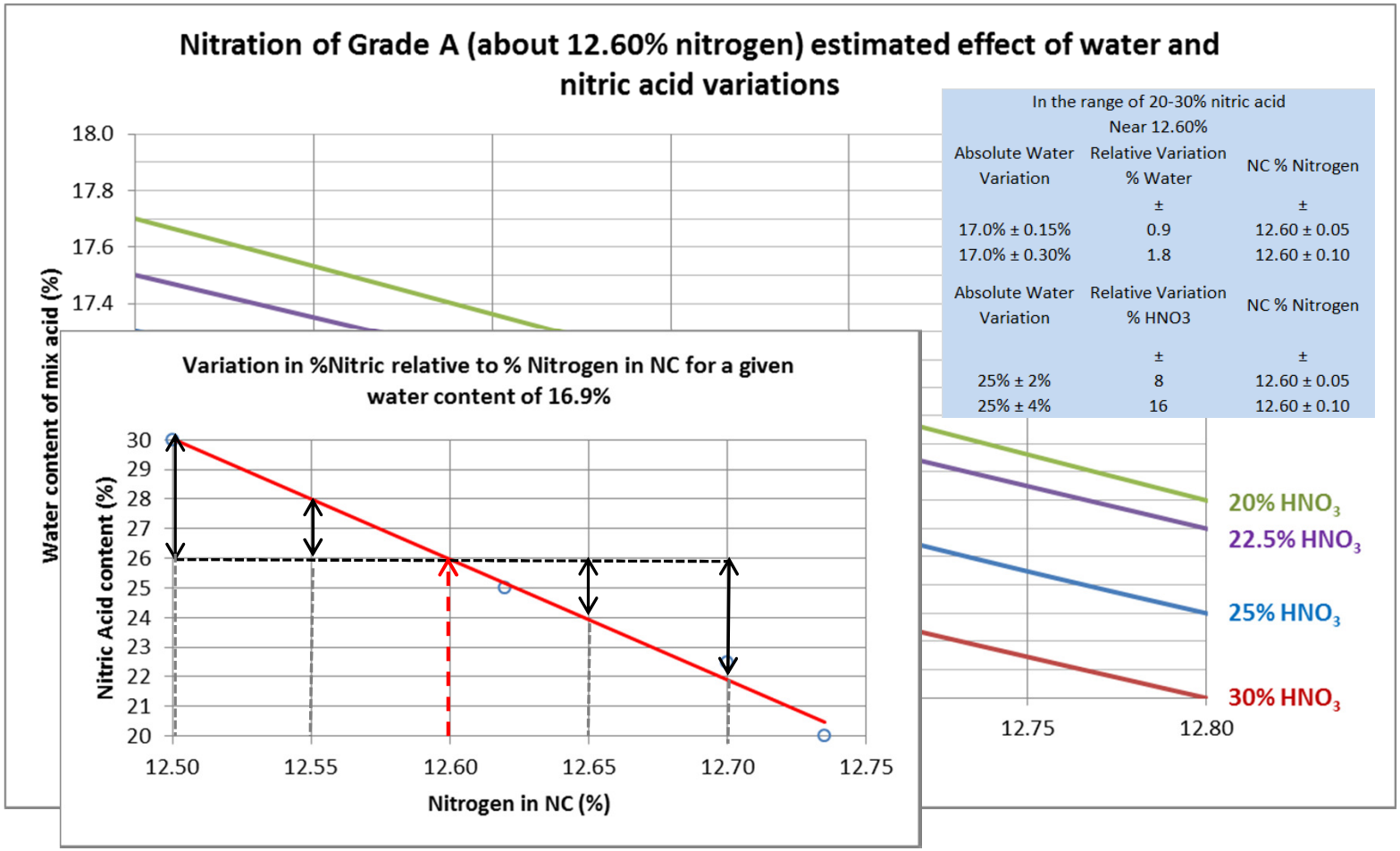
NC nitrating acid: Establishing tolerance



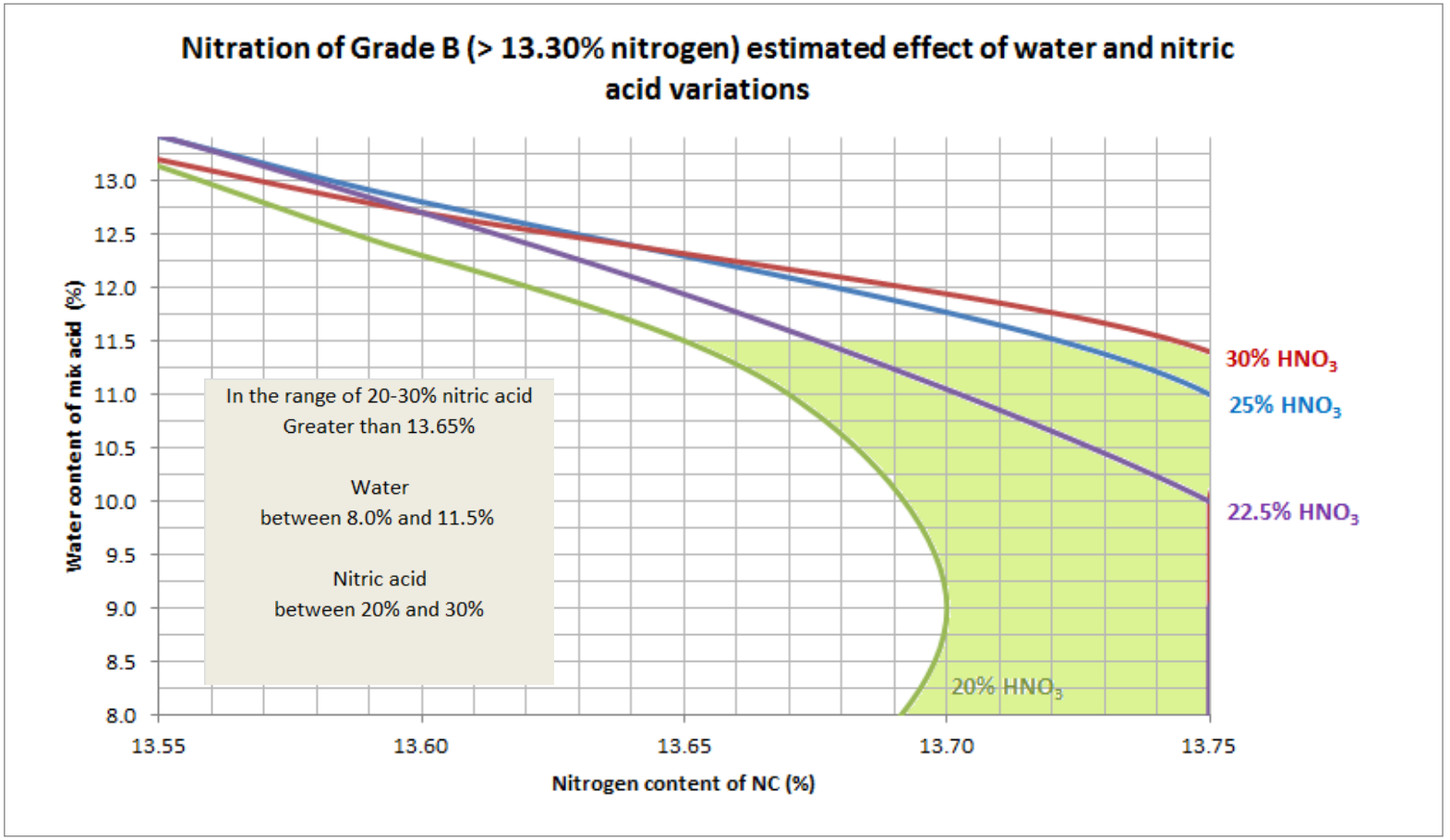
NC nitrating acid: Establishing tolerance



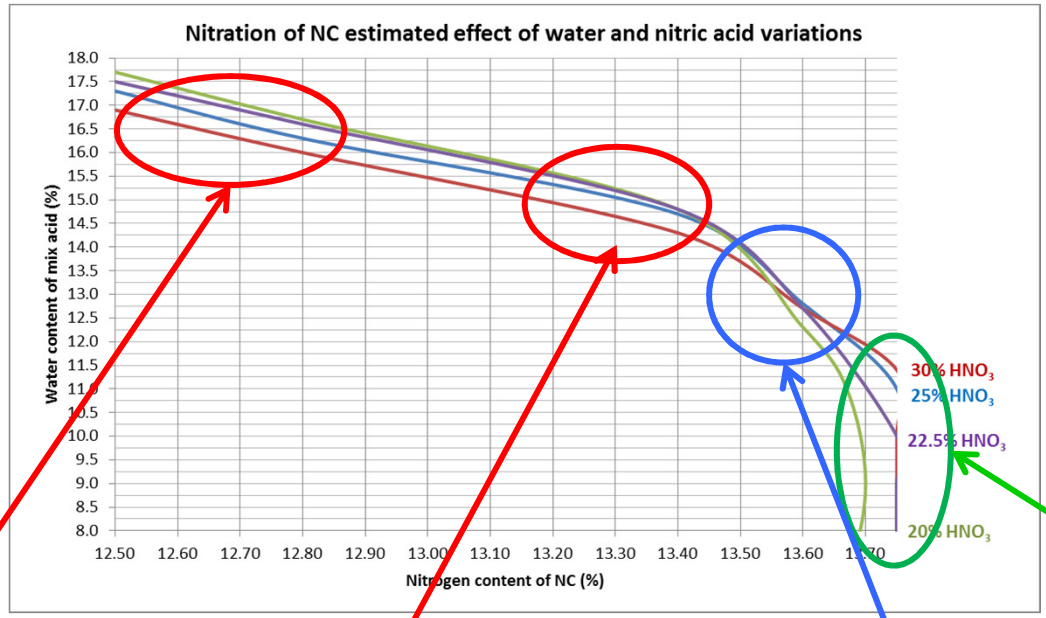
NC nitrating acid: Establishing tolerance



NC nitrating acid: Establishing tolerance



NC nitrating acid: Establishing tolerance



In the range of 20-30% nitric acid Near 12.60%		
Absolute Water Variation	Relative Variation % Water	NC % Nitrogen
	±	±
17.0% ± 0.15%	0.9	12.60 ± 0.05
17.0% ± 0.30%	1.8	12.60 ± 0.10
Absolute Water Variation	Relative Variation % HNO3	NC % Nitrogen
	±	±
25% ± 2%	8	12.60 ± 0.05
25% ± 4%	16	12.60 ± 0.10

In the range of 20-30% nitric acid Near 13.30%		
Absolute Water Variation	Relative Variation % Water	NC % Nitrogen
	±	±
15.0% ± 0.15%	1.0	13.30 ± 0.05
15.0% ± 0.30%	2.0	13.30 ± 0.10
Absolute Water Variation	Relative Variation % HNO3	NC % Nitrogen
	±	±
25% ± 2%	8	13.30 ± 0.05
25% ± 4%	16	13.30 ± 0.10

In the range of 20-30% nitric acid Near 13.55%		
Absolute Water Variation	Relative Variation % Water	NC % Nitrogen
	±	±
13.0% ± 0.6%	5	13.55 ± 0.05
13.0% ±1.2%	10	13.55 ± 0.10
Absolute Water Variation	Relative Variation % HNO3	NC % Nitrogen
	±	±
25% ± 5%	20	13.55 ± 0.05
25% ± 10%	40	13.55 ± 0.10

In the range of 20-30% nitric acid
Greater than 13.65%

Water
between 8.0% and 11.5%

Nitric acid
between 20% and 30%

NC nitrating acid nominal composition

Nitrating acid compose of 5 major constituents

- Sulfuric acid H_2SO_4
- Nitric acid HNO_3
- Water
- Nitrosyl sulphuric acid (or nitroso) $HNOSO_4$ *in water $HNOSO_4 \rightarrow HNO_2$ and H_2SO_4*
- Organic solid / dissolved

Total Acidity TA (express as H_2SO_4) = Total Sulfuric TS (express as H_2SO_4) + Total Nitric TN (express as H_2SO_4)

and

Total Sulfuric TS (express as H_2SO_4) = Actual Sulfuric AS (express as H_2SO_4) + Actual Nitroso ANO (Express as H_2SO_4)

Total Nitric TN (express as H_2SO_4) = Actual Nitric AN (express as H_2SO_4) + Actual Nitroso ANO (Express as H_2SO_4)

For precise quantification: $HNOSO_4$ correction must be applied to H_2SO_4 and HNO_3 quantification

The calculations yield:

Actual Sulfuric AS (express as H_2SO_4)

Actual Nitric AN (express as HNO_3)

Actual Nitroso NO (express as $HNOSO_4$)

And Water = 100 - AS (express as H_2SO_4) - AN (express as HNO_3) - ANO (express as $HNOSO_4$)

Sulfuric, Nitric and Water is often normalized to 100%
(as in most graphs of composition acid mixture relative to nitrogen content in NC).

Water compounds the error and variations of all the other methods

NC nitrating acid common analysis

TA = HNO_3 from AN + HNO_2 from NO + H_2SO_4 from AS + H_2SO_4 from NO

Total Acidity TA (express as H_2SO_4) = Titration in water with NaOH to pH 7.0

TS = H_2SO_4 from AS + H_2SO_4 from NO

Total Sulfuric TS (express as H_2SO_4) = Evaporation of nitric acid on steam bath

TN = HNO_3 for AN + HNO_2 from NO

Total Nitric TN (express as H_2SO_4 or HNO_3) = Mercury Nitrometer or Evaporation of nitric acid on steam bath

AN = HNO_3 for AN

Actual Nitric TN (express as H_2SO_4 or HNO_3) = Titration in concentrated sulfuric acid with Ferrous titrant (mV)

TNO = HNO_2 from NO + Organic matter oxidized by oxidizer titrant

Total Nitroso TNO (express as $HNOSO_4$ or H_2SO_4 or HNO_3) = Titration in water at room temperature with $KMnO_4$ (auto indicator or mV)

ANO = HNO_2 from NO

Actual Nitroso ANO (express as $HNOSO_4$ or H_2SO_4 or HNO_3) = Titration in water at cold (near 0°C) with $KMnO_4$ (auto indicator or mV)

Water (express as H_2O) → Numerous attempts to direct quantification –results inaccurate

-$HNOSO_4$ correction are to be applied to H_2SO_4 and HNO_3 determination for precise quantification of water

-Organic matters interfere with the quantification by $KMnO_4$ titration of the $HNOSO_4$ (variation is seasonal)

Required precision of analysis

Nitric acid quantification: some method detect AN others TN

Actual Nitric → -Ferrous titration

Total Nitric → -Evaporation of nitric or Mercury nitrometer

Those can corroborate only when taking Nitroso into consideration → Nitroso corrected for organic matter

Organic matters interfere with the quantification by $KMnO_4$ titration of the $HNOSO_4$

TNO = HNO_2 from NO + Organic matter oxidized by oxidizer titrant

Nitroso corrected for oxidizable organic matter: important for large nitroso and/or organic content

Two methods to correct from organic matter oxidation:

First:

A → Boiling and titration with oxidizer ($KMnO_4$) = Organic + HNO_2 from NO = **Total Nitroso TNO**

B → Urea (eliminate HNO_2), boiling and titration with oxidizer ($KMnO_4$) = Organic

A – B = HNO_2 from NO = **Actual Nitroso ANO**

Second:

Titrate in medium below 0°C to prevent organic oxidation by titrant = HNO_2 from NO = **Actual Nitroso ANO**

-Medium is water acidified with sulfuric acid as anti-freeze agent – kept in freezer at -10 to -14°C

-Titration is perform in about 5 minutes and final temperature is near 0°C

NC nitrating acid common analysis

3 important components to control the nitrating acid: Nitric / Sulfuric / Water

Expected precision of determination related to number of analysis required to obtain the result

ANO is obtained by applying 1 analytical methods:

-ANO directly by cold titration with $KMnO_4$

AN is obtained by applying an equivalent of 1 or 2 analytical methods:

-AN directly by ferrous titration or

-TN using Nitrometer and NO titration or

-TN using Nitric evaporation and NO titration

AS is obtained by applying an equivalent of 2 or 4 analytical methods:

-TS by Nitric evaporation and NO titration (once)

-TA by NaOH titration and TN by nitrometer and NO titration (once)

-TA by NaOH titration and AN by ferrous titration and NO titration (twice)

Water is obtained by applying an equivalent of 4 to 7 analytical methods:

- Obtained from Water = (100 - AN - AS - ANO)

NC nitrating acid common analysis

3 important components to control the nitrating acid: Nitric / Sulfuric / Water

Expected precision of determination related to number of analysis required to obtain the result

For addition or subtraction: the expected variation of final result V_R is obtained using the absolute variations V_N of the individual methods:

$$V_R = \sqrt{V_2^2 + V_3^2 + V_4^2 + \dots V_N^2}$$

Where;

V_N is the expected absolute variation from each individual methods contributing to the final result V_R

Note: for multiplication and division, the V_N is the percent relative variation instead

Example

Water = (100 - AN - AS - ANO)

Assuming:

AN	=	28.60 % ± 0.06 %
AS	=	61.90 % ± 0.10 %
ANO	=	1.50 % ± 0.02 %

The expected variation on the water content is:

$$V_W = \sqrt{V_{AN}^2 + V_{AS}^2 + V_{ANO}^2} = \sqrt{0.06^2 + 0.10^2 + 0.02^2} = 0.12\%$$

Thus water is expected to be 8.00 % ± 0.12 %

NC nitrating acid common analysis

3 important components to control the nitrating acid: Nitric / Sulfuric / Water

Method:	*Typical relative accuracy:*	*Typical absolute variation Example in GD-Valleyfield for a NC at 13.45% :*
AN by Ferrous titration	Better than 0.2%	28.60% ± 0.06 %
ANO by Cold $KMnO_4$ titration	Better than 1%	1.50% ± 0.02 %
TS by Evaporation of nitric	Better than 0.2%	63.05% ± 0.13 %
TN by Evaporation of nitric	Better than 0.2%	29.35% ± 0.06 %
TA by NaOH titration	Better than 0.1%	85.90% ± 0.09%
TN by Nitrometer	Better than 0.2%	28.60% ± 0.06 %
What is required to keep NC nitrogen content within ±0.1% for NC between 12.50% and 13.45% nitrogen:		
Water content (by difference)	Better than 2%	8.00 % ± 0.16%
What was achieved under –properly adjusted analytical conditions at GD-Valleyfield:		
Water content (by difference)	Between about 1.3% and 2.0%	8.00 % ± between 0.10% and 0.16 %

In conclusion:

Precision and accuracy of lab analysis of NC mix acid is paramount if process is to achieve performance.

The requirement is maximum for caustic titrations and nitric analysis both for proper estimation of water content.