Mass spectrometry system: The ionspray voltage and ion source temperature were set at 5500 V and 450 °C. Pure nitrogen was used as auxiliary, curtain, and collision gas and air was used as nebulizer gas. Samples were separated on a C18 column (2.1 mm ID × 50 mm, 3 μm) (VisionHT C18 CL; Grace Vydac, Hesperia, CA, U.S.) using a gradient flow of 0.2 mL/min with 0.1% FA in water (A) and 0.1% FA in ACN (B) as mobile phases. The LC gradient was increased from 5% B to 10% B for 10 min, from 10% B to 30% B for 15 min, from 30% B to 99% B for 1 min where it was kept for 1 min. The column was re-equilibrated at 5% B for 5 min before the next sample was injected. The MRM detection window and target scan time were set to 90s and 4s, respectively and unit resolution were used for Q1 and Q3. Collision energy (CE) and declustering potential (DP) values were calculated according to:

- doubly charged precursors: $CE = 0.057m/z - 4.300$
- triply charged precursors: $CE = 0.038m/z + 2.187$
- doubly and triply precursors: $DP = 0.0716m/z + 33.739$

where $m/z$ is the mass-to-charge ratio of the precursor ion.

SRM analyses of NLF proteins: The SRM assays targeting NLF proteins were developed in a previous study. For the present study some modifications were made to the original method. In order to shorten the analysis time, the LC gradient was modified leading to a reduction of the analysis time from 45 min to 32 min. Therefore, the SRM assays of the original method had to be adjusted. Unscheduled MS/MS methods containing about 200 transitions each were acquired (dwell time 20 ms). To make sure that the correct peptide was targeted additional transitions were added to the original assays (at least 5 per peptide). The data was analyzed in Skyline (Version 1.4.0) and the retention times and in some cases also choice of transition, were adjusted to the new LC gradient. A pooled, digested NLF sample was used for data acquisition of the previously developed assays and the new ones. Also, two
proteins, submaxillary gland androgen-regulated protein 3B (P02814) and Ig heavy chain V-III region KOL (P01772), that were previously identified in NLF (unpublished data) were added to the SRM method. The SRM assays for these proteins were developed in accordance with previous work.¹⁴

**SRM analyses of oxidized peptides:** SRM assays targeting oxidized peptides were developed using Skyline (Version 1.4.0).¹⁵ Transitions with precursor ions (charge: +2 and +3) and y- and b-ion fragments in the m/z range 300-1250 were selected. The selection of transitions was when possible based on two human MS/MS libraries (collision cell and ion trap data) downloaded from the National Institute of Standards and Technology (http://peptide.nist.gov/, downloaded June 12th 2013). The transitions with highest ranks were chosen and when no MS/MS data was available, all transitions were selected. Unscheduled MS/MS methods with about 400 transitions each (dwell time 10 ms) were acquired. Precursors with at least five co-eluting transitions were kept and the transitions of highest intensities, three per peptide, were selected for the final SRM method.